

## Synthesis and Structure of (*N,N,N',N'*-Tetrakis(2-pyridylmethyl)ethylenediamine)dicationic and Its Dicarbonyl Adduct

ROBERT R. GAGNÉ,\* ROBERT P. KREH, JOHN A. DODGE, RICHARD E. MARSH, and MICHAEL McCOOL

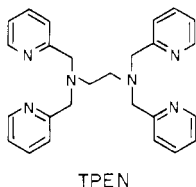
Received June 9, 1981

Reaction of the ligand *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) with  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$  produces a binuclear complex,  $\text{Cu}_2(\text{TPEN})^{2+}$ . This complex reversibly binds 2 equiv of carbon monoxide, giving an adduct that displays a pair of CO stretching absorptions at 2097 and 2107  $\text{cm}^{-1}$ . Both compounds have been examined by single-crystal X-ray diffraction. Each copper atom of  $\text{Cu}_2(\text{TPEN})(\text{BF}_4)_2$  is bound in a highly asymmetric environment, with an intramolecular copper-copper separation of 2.78 Å. In the carbonyl adduct the metal-ligand bonds have rearranged, each copper has assumed a pseudotetrahedral geometry, and there is no longer any direct metal-metal interaction. Crystal data are as follows: for  $\text{Cu}_2(\text{TPEN})(\text{BF}_4)_2$ , space group  $C2/c$ ,  $a = 13.099$  (4) Å,  $b = 15.974$  (6) Å,  $c = 14.472$  (5) Å,  $\beta = 102.74$  (2)°,  $V = 2953.7$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.051$  for 665 reflections with  $F_o^2 > 3\sigma(F_o^2)$ ; for  $\text{Cu}_2(\text{TPEN})(\text{CO})_2(\text{BF}_4)_2$ , space group  $P2_1/c$ ,  $a = 17.706$  (5) Å,  $b = 10.372$  (3) Å,  $c = 19.601$  (5) Å,  $\beta = 112.77$  (2)°,  $V = 3319.2$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.042$  for 2271 reflections with  $F_o^2 > 3\sigma(F_o^2)$ .

### Introduction

Copper(I) complexes show a variety of coordination environments ranging in coordination number from 2 to 5.<sup>1,2</sup> The number of ligands bound to the univalent metal seems to be influenced greatly by both the chemical nature of the ligands and the geometry they impose. We recently reported a series of binuclear copper(I) complexes that are three-coordinate in the solid state and display an additional intermolecular copper-copper interaction (shorter than the intramolecular separation between metals).<sup>3</sup> These complexes appear to be three-coordinate in solution as well, with no intermolecular interaction. In spite of the presence of an available (fourth) coordination site at each metal, the compounds are unreactive toward ligands such as pyridine and carbon monoxide. (See Discussion.)

In contrast, a stable carbon monoxide adduct is formed with the binuclear copper(I) complex derived from the ligand *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN).

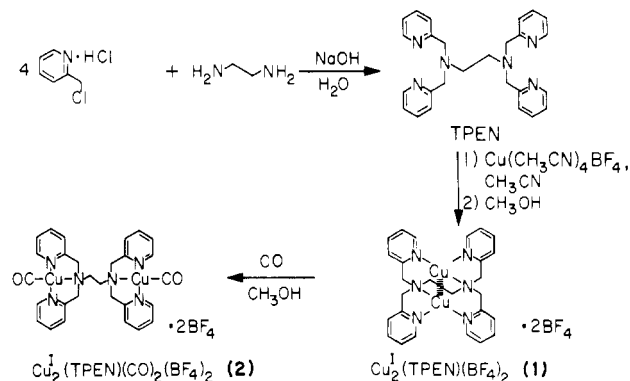


To facilitate comparison of the systems, we have undertaken complete crystal structural analyses of both  $\text{Cu}_2(\text{TPEN})(\text{BF}_4)_2$  (**1**) and its dicarbonyl adduct,  $\text{Cu}_2(\text{TPEN})(\text{CO})_2(\text{BF}_4)_2$  (**2**). These structures show that the TPEN ligand is capable of binding a pair of cuprous ions in two distinctly different fashions. In compound **1**,  $\text{Cu}_2(\text{TPEN})(\text{BF}_4)_2$ , there is a significant intramolecular copper-copper interaction, with the ligand folded over on itself, but in the carbonyl adduct, **2**, the copper-nitrogen bonds have undergone extensive rearrangement and there is no direct Cu-Cu interaction.

### Synthesis and Characterization of Complexes

The methods used in preparing the ligand and its cuprous complexes are outlined in Scheme I. Compound **1**,  $\text{Cu}_2$ -

Scheme I

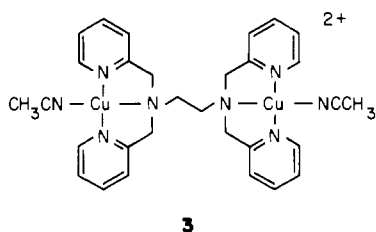


(TPEN)( $\text{BF}_4$ )<sub>2</sub>, is only slightly soluble in methanol, but saturation of a methanol suspension with carbon monoxide results in complete dissolution. Upon purging of this colorless solution with nitrogen, compound **1** (identified by IR) is reprecipitated. This process is totally reversible and may be repeated at will. Evaporation of the methanol with a stream of CO gives off-white crystals of the dicarbonyl,  $\text{Cu}_2(\text{TPEN})(\text{CO})_2(\text{BF}_4)_2$  (**2**).

Shown in Figure 1 are the structures of the complex cations of compounds **1** and **2**, as determined by single-crystal X-ray diffraction. In compound **1** each copper atom is bound between two pyridine rings, while forming a much weaker third bond with one of the tertiary amine nitrogens. The two pyridine rings in this case originate from different nitrogens of the ethylenediamine moiety. Significant interaction between the two copper atoms themselves is indicated by the metal-metal separation of 2.78 Å. In compound **2** an additional ligand, carbon monoxide, has moved into the inner coordination sphere of each copper, and the direct metal-metal interaction no longer occurs. Each copper atom has assumed a pseudotetrahedral geometry, with the other three bound groups consisting of an amine nitrogen and the two pyridylmethyl groups attached to it. These structures are described in further detail in the following sections.

Compound **1** is pale green in appearance in the solid state, but the visible spectrum of the solid (Nujol mull, under He) shows no absorption above 450 nm. Although the compound is insoluble in most organic solvents (e.g.,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{OH}$ ), it is very soluble in acetonitrile, forming a deep yellow solution. This color change upon dissolution may be indicative of coordination of  $\text{CH}_2\text{CN}$  to copper to give a structure similar to that observed for the carbonyl adduct (structure **3**).

- Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115-163. Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1-95. Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1977**, *23*, 131-144.
- Gagné, R. R.; Allison, J. L.; Gall, R. S.; Koval, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7170-7178.
- Gagné, R. R.; Kreh, R. P.; Dodge, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6917-6927.



Compound **1** also dissolves in *N,N*-dimethylformamide, but the solution immediately turns blue and copper metal is plated out. This disproportionation reaction can be reversed entirely by purging the solution with carbon monoxide, resulting in a colorless solution, which presumably contains the carbonyl adduct, **2**.

As expected, compound **1** is diamagnetic and gives very sharp proton NMR signals (Figure 2). In Table I are listed the chemical shifts for both complex **1** and the free ligand in CD<sub>3</sub>CN solution. These spectra confirm the identity of the organic entity. The binding of copper(I) is evidenced in the spectrum of the complex by the rather large changes in the chemical shifts relative to the free ligand. The resonances due to the methylene protons ( $\alpha$  and  $\beta$ ) and to three of the pyridine protons (py<sub>4</sub>, py<sub>5</sub>, and py<sub>6</sub>) all move downfield upon binding of the positive metal ion.<sup>4</sup> The py<sub>3</sub> resonance, on the other hand, shows an upfield shift. This anomalous behavior could be the result of pyridine ring-current effects.

The infrared spectrum of the carbonyl complex, **2**, has been examined both in solution and in the solid state. In methylene chloride solution a single carbonyl stretching band is observed at 2110 cm<sup>-1</sup>. This frequency is very high compared to those found in other copper(I) carbonyl complexes.<sup>2,5,6</sup> The cationic character and the "soft" pyridine ligands of **2** may result in less  $\pi$  donation from copper(I) into the  $\pi^*$  orbital of CO, thereby raising the frequency of the CO stretch. The solid-state IR spectrum of **2** (Nujol mull) exhibits a strong, sharp pair of CO bands at 2097 and 2107 cm<sup>-1</sup>, consistent with the observation of two nonequivalent carbonyl groups in the crystal structure of the compound (vide infra).

While neither Cu<sub>2</sub>(TPEN)(BF<sub>4</sub>)<sub>2</sub> nor its carbonyl adduct shows reactivity toward oxygen in the solid state, solutions of the latter (**2**) in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>OH, or DMF change from colorless to blue. This reaction cannot be reversed by purging the solutions with argon. The autoxidation products have not been characterized.

#### Crystallographic Analysis of Cu<sub>2</sub>(TPEN)(BF<sub>4</sub>)<sub>2</sub> (**1**)

Table II summarizes the basic crystal data for both compounds **1** and **2**. The atomic labeling scheme for Cu<sub>2</sub>(TPEN)<sup>2+</sup> is shown in Figure 3. The dication lies on a crystallographic twofold rotation axis, and primes are used to designate symmetry-related atoms within the same complex. The atomic parameters and interatomic distances and angles are given in Tables III–VI.

The outstanding feature of the structure of the Cu<sub>2</sub>(TPEN)<sup>2+</sup> cation is its extreme compactness (see Figures 1 and 3). The gauche conformation of the ethylenediamine "backbone" (N–C–C–N torsion angle = 52°) permits each cuprous ion to coordinate to pyridine groups from opposite ends of the ethylenediamine chain and more importantly allows the close intramolecular copper–copper contact of 2.779 (2) Å.

**Table I.** Proton NMR Frequencies for TPEN and Cu<sub>2</sub>(TPEN)(BF<sub>4</sub>)<sub>2</sub><sup>a</sup>

compd	$\alpha$	$\beta$	py <sub>3</sub>	py <sub>4</sub>	py <sub>5</sub>	py <sub>6</sub>
TPEN	3.68	2.63	7.39	7.62	7.11	8.44
Cu <sub>2</sub> (TPEN)(BF <sub>4</sub> ) <sub>2</sub>	3.72	2.98	7.23	7.77	7.34	8.55

<sup>a</sup> All spectra were obtained in CD<sub>3</sub>CN solution at 34 °C under an atmosphere of helium. The values listed are given in  $\delta$ , relative to Me<sub>4</sub>Si. The assignments for the resonances are given in Figure 1.

**Table II.** Crystal Data for Cu<sub>2</sub>(TPEN)(BF<sub>4</sub>)<sub>2</sub> (**1**) and Cu<sub>2</sub>(TPEN)(CO)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> (**2**)

compd	Cu <sub>2</sub> (TPEN)(BF <sub>4</sub> ) <sub>2</sub>	Cu <sub>2</sub> (TPEN)(CO) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub>
formula	C <sub>26</sub> H <sub>28</sub> B <sub>2</sub> Cu <sub>2</sub> F <sub>8</sub> N <sub>6</sub>	C <sub>28</sub> H <sub>28</sub> B <sub>2</sub> Cu <sub>2</sub> F <sub>8</sub> N <sub>6</sub> O <sub>2</sub>
(per asym unit)		
fw	725.25	781.27
space group	C2/c (No. 15)	P2 <sub>1</sub> /c (No. 14)
<i>a</i> , Å	13.099 (4)	17.706 (5)
<i>b</i> , Å	15.974 (6)	10.372 (3)
<i>c</i> , Å	14.472 (5)	19.601 (5)
$\beta$ , deg	102.74 (2)	112.77 (2)
<i>V</i> , Å <sup>3</sup>	2953.7 (17)	3319.2 (16)
<i>Z</i>	4	4
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	1.63	1.56
$\mu$ , cm <sup>-1</sup>	15.8	23.7
radiation	Mo K $\alpha$	Cu K $\alpha$
$\lambda$ , Å	0.71069	1.5418

The coordination about copper (crystallographically identical for the two atoms) is difficult to place in a particular geometric category. As suggested by Figures 1 and 3, each metal ion deviates only slightly (0.07 Å) from the plane defined by the three nitrogen atoms to which it is bound, the direction of this deviation being that which gives the shorter Cu–Cu' distance. The bonds to the two pyridine nitrogens form a large, but not linear, angle about copper of 146.8°, and the lengths of these bonds are at the low end of the range usually found for Cu<sup>I</sup> coordinated to nitrogen (Cu–N1 = 1.94 Å, Cu–N16' = 1.89 Å).<sup>2,3,5,6</sup> The third metal–nitrogen bond (Cu–N8) is much longer than the other two, at 2.30 Å, and must be considerably weaker. The angles about copper associated with these interactions are given in Table VI.

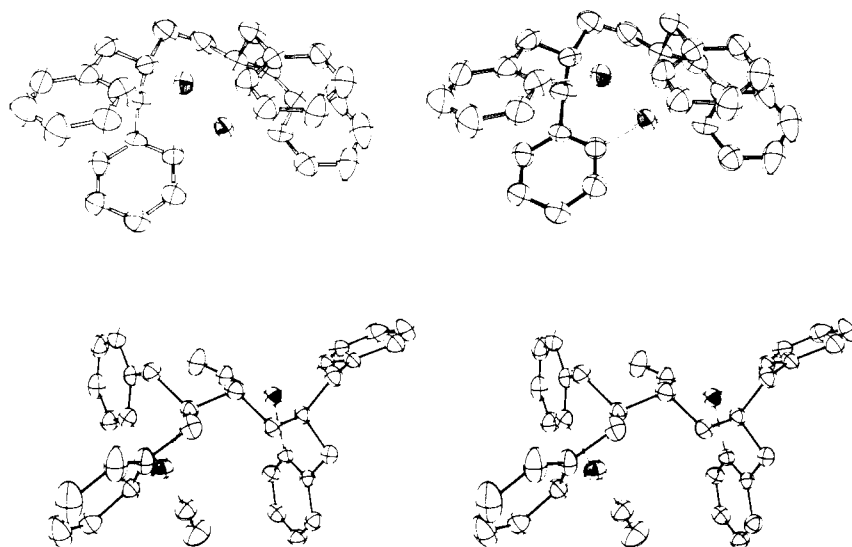
There are several factors that may contribute to the skewing of complex **1**, i.e., the twisting of the ethylenediamine chain and canting of the Cu–Cu' axis. The observed conformation of the TPEN ligand does aim the lone electron pair of the amine nitrogen N8 in the direction of Cu; angles at N8 are Cu–N8–C7 = 97.9°, Cu–N8–C9 = 114.8°, and Cu–N8–C10 = 113.6°. Steric factors may also be important. Of course, the skewing of the ligand does avoid total eclipsing of the pyridine rings (see bottom of Figure 3). The gauche conformation about the C9–C9' bond is expected from basic steric considerations, and space-filling models suggest it is also necessary to allow the pyridine rings to move far enough apart to accommodate the copper atoms. The observed conformation about the N8–C9 bond (and the equivalent N8'–C9' bond) not only allows the nitrogen lone pairs to point toward copper atoms but also relieves van der Waals repulsions among hydrogen atoms (e.g., among H7A, H9A, and H10A'), all of which would point upward in the upper drawing of Figure 3).

The BF<sub>4</sub><sup>-</sup> counterions of compound **1** have been represented as disordered between two discrete positions, although the separation between some pairs of partial atoms is sufficiently small that representation as a single anisotropic atom would probably have been as satisfactory. In the model used, each BF<sub>4</sub><sup>-</sup> group occupies two positions, which differ primarily by rotation of the group with a small degree (ca. 0.5 Å) of translation. The populations of these sites are approximately 0.71 and 0.29. No fluorine atom lies within 3.5 Å of a copper atom.

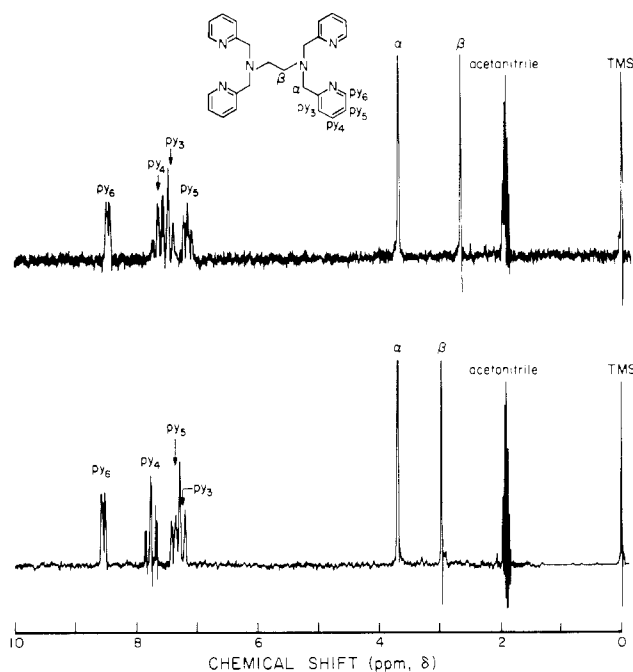
(4) Similar downfield shifts have been observed for imidazole protons upon binding of the imidazole nitrogen to a cuprous ion: Sugiura, Y. *Inorg. Chem.* **1978**, *17*, 2176–2182.

(5) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191–1197.

(6) Bruce, M. I.; Ostaszewski, A. P. *J. Chem. Soc., Dalton Trans.* **1973**, 2433–2436. Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Abu Salah, O. M.; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051–2056.



**Figure 1.** Stereodrawings of  $\text{Cu}_2(\text{TPEN})^{2+}$  (top) and  $\text{Cu}_2(\text{TPEN})(\text{CO})_2^{2+}$  (bottom).

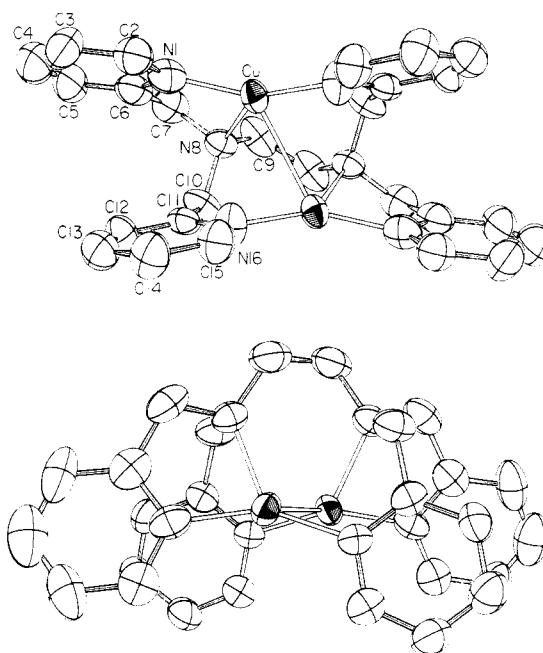


**Figure 2.** NMR spectra of the TPEN ligand (top) and  $\text{Cu}_2(\text{TPEN})(\text{BF}_4)_2$  (1) (bottom) in  $\text{CD}_3\text{CN}$  at  $34^\circ\text{C}$ .

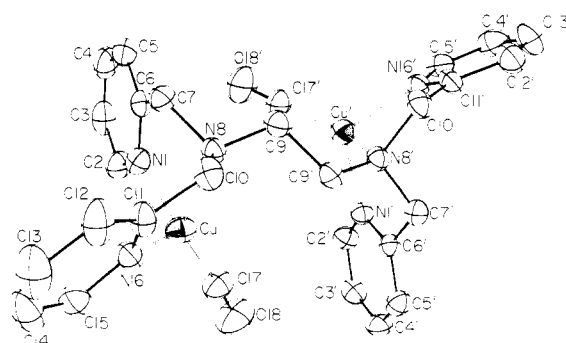
### Crystallographic Analysis of $\text{Cu}_2(\text{TPEN})(\text{CO})_2(\text{BF}_4)_2$ (2)

A drawing of the  $\text{Cu}_2(\text{TPEN})(\text{CO})_2^{2+}$  cation, along with the numbering scheme to be used, is shown in Figure 4. Bond lengths and angles are listed in Tables V and VI. Although the complex contains two copper ions in effectively identical chemical environments, in this case the two are not related by crystallographic symmetry. Indeed, there are some tantalizing differences between the geometries of the two halves of the complex that will be discussed later.

The ethylenediamine group of the TPEN ligand is more extended than in compound 1, with a torsion angle  $\text{N}-\text{C}-\text{C}-\text{N}$  of  $152^\circ$ . The copper atoms, which are connected to one another only by the ethylenediamine bridge, are far apart. The four copper–pyridine nitrogen bonds are of statistically equivalent length, averaging  $2.035(3) \text{ \AA}$ . This distance is considerably greater than for the corresponding bonds in compound 1. The copper–amine nitrogen bonds, on the other hand, are considerably shorter than in 1, although the average length of  $2.164(4) \text{ \AA}$  is still rather long. Thus, the geometry about copper in 2 is distorted from tetrahedral but is much



**Figure 3.** ORTEP drawings of  $\text{Cu}_2(\text{TPEN})^{2+}$ , including the atomic labeling scheme. Ellipsoids of 40% probability are shown. The twofold axis is perpendicular to the page in the upper diagram and parallel to it in the lower.



**Figure 4.** ORTEP drawing of  $\text{Cu}_2(\text{TPEN})(\text{CO})_2^{2+}$ , including the atomic labeling scheme. Although primes are used here, this molecule does not contain a twofold rotation axis.

more symmetric than in 1. The structures of both compounds suggest that the cuprous ion has a lower affinity for the “hard” tertiary amine nitrogen than for pyridine.

The geometries of the CO ligands are especially interesting. While the C–O distances, at 1.10 (1) and 1.11 (1) Å, are statistically equivalent, the Cu–C distances, 1.809 (7) and 1.781 (7) Å, differ by nearly three esd's. This difference would not be particularly noteworthy except for the observation of two distinct CO bands in the solid-state IR spectrum. The difference between the two frequencies of 10 cm<sup>-1</sup> would be expected to correspond to a difference in C–O bond lengths of less than 0.01 Å, which is within our experimental error, but the implied change in electron distribution could well result in a much larger difference in the lengths of the Cu–C bonds, as observed. Hence, there appears to be a real difference between the bonding characteristics of CO in the two halves of the complex.

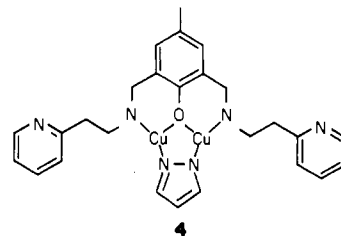
In seeking further insight into this difference, we note that the C17'–O18' ligand nestles appreciably closer to a neighboring pyridine ring (N1–C6) than does C17–O18: the shortest interatomic distance, O18'...C4, at 3.38 Å, is nearly 0.3 Å shorter than O18...C4', 3.66 Å; the distance from O18' to the center of the pyridine ring, 3.34 Å, compares with the value 3.53 Å for O18. Thus, the shorter O...pyridine contact corresponds to the shorter Cu–C bond and to the marginally longer C–O bond. Just possibly there are sufficient electronic interactions between O18' and the pyridine ring to be reflected in a slight perturbation to the C–O and Cu–C bonds; we see no other reason for the apparent asymmetry, as there are no unusual intermolecular contacts.<sup>7</sup>

Of the two tetrafluoroborate anions of compound 2, one is disordered and the other is ordered, although with significant anisotropic motions of the fluorine atoms. In the former group four of the atoms (B2, F5, F6, F7) are distributed over positions sufficiently close (0.5 Å or less) that anisotropic temperature factors are adequate to describe their electron distributions. The remaining fluorine atom has a 50% occupancy of each of two positions (F8A and F8B), which are separated by about 1.2 Å.

## Discussion

The apparent preference of cuprous ions for lower coordination numbers (i.e., 2, 3 and 4)<sup>1,3</sup> suggested the possibility of the hexadentate TPEN performing as a bridging ligand between two coppers. The structure of the binuclear complex that was isolated was somewhat surprising, however. It had been thought that each metal might bind to an amine nitrogen and the two pyridylmethyl groups attached to it, possibly with the BF<sub>4</sub><sup>-</sup> groups acting as fourth ligands. Instead, the pyridine rings that are bound to each copper originate from different nitrogens of the ethylenediamine group. There are bonds with the amine nitrogens as well, but these are quite long. The observed structure does not facilitate this copper–amine interaction, compared to other conceivable structures, whereas it does facilitate the copper–copper interaction. In fact, the peculiar conformation of the ligand and the surprisingly asymmetric bonding about the copper atoms seem to reflect a determination of the complex to form a Cu–Cu bond despite severe steric handicaps.

The coordination about copper observed for Cu<sub>2</sub>(TPEN)(BF<sub>4</sub>)<sub>2</sub> (1) bears some similarity to that which we recently reported for compound 4, formed with another



multidentate ligand.<sup>3</sup> Both structures indicate a preference of copper(I) toward a somewhat linear arrangement of two nitrogen ligands.<sup>9,12</sup> This was manifested in 4 by the short Cu–N distances (all close to 1.89 Å), the rather long Cu–O distances (both about 2.09 Å), and the large N–Cu–N angles (both close to 169°). Note, however, that in both cases the third ligand (amine nitrogen or phenolate oxygen) is rather “hard” and thus unfavorable for copper(I). Therefore, the partial two-coordinate character of these compounds may simply be an avoidance of undesirable ligands. It should also be noted that systems 1 and 4 both foster a direct Cu–Cu interaction.<sup>9,13</sup> (In the case of compound 4 this interaction is intermolecular in the solid state. The molecules stack to give a Cu–Cu separation of 2.97 Å, compared with an intramolecular separation of 3.30 Å.)

In the presence of carbon monoxide, compound 1 undergoes extensive ligand rearrangement to form the dicarbonyl, 2. The crystal structure of 2 exhibits the “expected” pseudotetrahedral geometry with all three nitrogen ligands for each copper coming from the same end of the ethylenediamine bridge. Thus, in the TPEN system the preferred coordination about copper depends on the presence or absence of a potential fourth ligand (CO or CH<sub>3</sub>CN). In contrast, compound 4 showed no tendency to bind CO or pyridine. From the judgement of molecular models, the reason for this difference is not that compound 4 cannot form a pseudotetrahedral geometry with a fourth ligand bound to copper. Evidently there is a special stabilization of cuprous ions in 4 that would be lost on binding another ligand.<sup>12</sup> The origin of this stability remains unclear, however.

The structures reported in this paper, as well as those of other cuprous systems,<sup>1–3</sup> demonstrate that a wide variety of coordination environments can be assumed by copper(I) ions. Obviously the number and geometry of ligands preferred by copper(I) are extremely sensitive to minor ligand alterations. These effects have not been well-defined, and as a result one must exercise caution in the prediction of structures for such systems.

## Experimental Section

**Materials.** All chemicals were reagent grade and were used as received unless otherwise noted. *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) was prepared by a modification of the literature method.<sup>14</sup> Tetrakis(acetonitrile)copper(I) tetrafluoroborate was also prepared by the published procedure.<sup>15</sup>

- (7) In the structure of the complex Cu<sub>2</sub>(en)<sub>3</sub>(CO)<sub>2</sub><sup>2+</sup>, which bears similarities to that of Cu<sub>2</sub>(TPEN)(CO)<sub>2</sub><sup>2+</sup>, each CO is distributed over two sites (on the same copper) with nearly equal populations; only one CO stretching frequency is observed.<sup>5</sup> Another similar structure is that of Cu<sub>2</sub>(histamine)<sub>3</sub>(CO)<sub>2</sub><sup>2+</sup>, but in this case the metals have different ligand environments and there are two CO bands (ν<sub>CO</sub> = 2055, 2066 cm<sup>-1</sup>).<sup>8</sup> The crystal structure of [hydrotris(1-pyrazolyl)borato]copper(I) carbonyl contains two nonequivalent molecules, but only one CO band is observed (ν<sub>CO</sub> = 2083 cm<sup>-1</sup>).<sup>6</sup>
- (8) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* 1979, 197–199.

- (9) Somewhat similar structures were observed for tetrakis[(1,3-dimethyltriazeno)copper(I)]<sup>10</sup> and bis[diazo(aminobenzene)copper(I)]<sup>11</sup> in which each copper is bound linearly to two nitrogens and, in addition, close Cu–Cu contacts were observed.
- (10) O'Connor, J. E.; Janusonis, G. A.; Corey, E. R. *J. Chem. Soc., Chem. Commun.* 1968, 445–446.
- (11) Brown, I. D.; Dunitz, J. D. *Acta Crystallogr.* 1961, 14, 480–485.
- (12) In general, two-coordinate copper(I) complexes are found with strong σ-donor nitrogen ligands (e.g., Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>) while four-coordination appears to be favored with π-acceptor nitrogen ligands (e.g., Cu(py)<sub>4</sub><sup>+</sup>): James, B. R.; Williams, R. J. P. *J. Chem. Soc.* 1961, 2007–2019.
- (13) Mehrotra and Hoffman have reported molecular orbital calculations that indicate a positive attraction between Cu<sup>I</sup> (d<sup>10</sup>) centers through the mixing in of metal s and p orbitals: Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* 1978, 17, 2187–2189.
- (14) Anderegg, G.; Wenk, F. *Helv. Chim. Acta* 1967, 50, 2330–2332.

Table III. Atomic Parameters and Esd's for the Nonhydrogen Atoms of  $\text{Cu}_2(\text{TPEN})(\text{BF}_4)_2$  (1) and  $\text{Cu}_2(\text{TPEN})(\text{CO})_2(\text{BF}_4)_2$  (2)

$\text{Cu}_2(\text{TPEN})(\text{BF}_4)_2$									
	$x^a$	$y$	$z$	$U_{11}^b$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu	3656 (9)	3694 (8)	16687 (9)	470 (8)	592 (8)	691 (9)	-81 (10)	59 (6)	28 (11)
N1	1769 (5)	191 (5)	1486 (5)	87 (6)	62 (7)	72 (6)	-18 (5)	10 (5)	-17 (5)
C2	2163 (8)	-550 (6)	1290 (6)	83 (6)	93 (10)	77 (8)	-3 (8)	16 (7)	1 (7)
C3	3216 (9)	-660 (7)	1271 (7)	95 (10)	150 (13)	97 (10)	33 (9)	46 (9)	15 (9)
C4	3879 (8)	1 (9)	1469 (8)	85 (9)	194 (17)	99 (10)	15 (9)	28 (8)	36 (10)
C5	3508 (9)	750 (7)	1679 (7)	67 (8)	166 (14)	94 (10)	-23 (9)	22 (8)	33 (9)
C6	2448 (8)	839 (6)	1698 (6)	87 (9)	90 (9)	59 (8)	-11 (8)	6 (7)	9 (7)
C7	1956 (8)	1664 (6)	1873 (7)	95 (9)	81 (9)	82 (9)	-29 (7)	15 (7)	18 (7)
N8	1124 (5)	1554 (4)	2418 (5)	76 (6)	58 (6)	58 (6)	-8 (5)	8 (5)	7 (5)
C9	451 (7)	2323 (5)	2247 (7)	91 (10)	56 (7)	121 (11)	-10 (6)	-18 (8)	9 (7)
C10	1601 (7)	1426 (6)	3447 (6)	96 (8)	57 (7)	71 (8)	-5 (6)	-15 (7)	6 (7)
C11	1864 (7)	525 (6)	3654 (5)	71 (7)	64 (8)	46 (6)	8 (7)	7 (6)	10 (6)
C12	2888 (7)	248 (6)	3909 (6)	59 (7)	81 (8)	86 (8)	-11 (7)	3 (6)	-2 (8)
C13	3100 (7)	-594 (6)	4080 (6)	82 (8)	93 (10)	88 (8)	16 (7)	17 (7)	20 (8)
C14	2245 (8)	-1129 (6)	4034 (7)	88 (9)	69 (8)	119 (10)	19 (7)	32 (8)	22 (8)
C15	1246 (8)	-793 (6)	3802 (7)	79 (8)	69 (8)	103 (9)	6 (7)	25 (7)	-1 (7)
N16	1045 (6)	14 (5)	3621 (5)	67 (6)	49 (6)	122 (8)	5 (5)	26 (5)	13 (6)
F1A	4136 (6)	2337 (5)	390 (6)	66 (6)	90 (7)	176 (9)	-4 (5)	20 (6)	-14 (6)
F2A	5526 (8)	2097 (8)	1446 (7)	114 (7)	305 (13)	66 (8)	1 (9)	16 (6)	-39 (8)
F3A	5387 (8)	1686 (6)	-118 (6)	149 (9)	111 (8)	102 (8)	51 (7)	20 (6)	-35 (6)
F4A	5484 (10)	3076 (7)	218 (8)	220 (12)	133 (10)	186 (11)	116 (9)	108 (9)	-37 (8)
	$x$	$y$	$z$	$B, \text{Å}^2$	$x$	$y$	$z$	$B, \text{Å}^2$	
F1B	473 (2)	283 (2)	14 (2)	13.8 (1.2)	F4B	627 (2)	234 (2)	17 (2)	11.6 (0.9)
F2B	587 (2)	251 (1)	136 (2)	10.3 (0.9)	BA	513 (0)	230 (0)	48 (0)	8.5 (0.7)
F3B	522 (2)	157 (2)	53 (2)	14.1 (1.1)	BB	552 (0)	231 (0)	55 (0)	6.2 (1.4)
$\text{Cu}_2(\text{TPEN})(\text{CO})_2(\text{BF}_4)_2$									
	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu	64488 (5)	12678 (9)	30151 (5)	569 (5)	670 (6)	633 (6)	-7 (5)	114 (5)	-10 (5)
Cu'	81118 (5)	27758 (8)	17656 (5)	574 (5)	604 (6)	655 (6)	4 (5)	208 (5)	-64 (5)
O18	5329 (3)	1361 (6)	1472 (3)	103 (4)	138 (5)	69 (4)	25 (4)	-13 (3)	-3 (4)
O18'	7923 (4)	5020 (6)	2558 (4)	142 (5)	107 (5)	166 (6)	14 (4)	62 (5)	-62 (4)
B1	3857 (5)	2529 (10)	3087 (6)	74 (6)	86 (8)	96 (8)	16 (6)	16 (6)	-16 (6)
B2	553 (5)	2391 (11)	4120 (6)	56 (6)	95 (9)	122 (9)	5 (6)	-2 (6)	8 (8)
F1	4497 (3)	2591 (7)	2889 (4)	128 (4)	246 (7)	190 (6)	16 (5)	92 (4)	35 (5)
F2	3888 (3)	3461 (6)	3576 (3)	131 (4)	178 (6)	136 (4)	21 (4)	8 (4)	-84 (4)
F3	3918 (3)	1372 (6)	3433 (3)	111 (4)	139 (5)	157 (5)	29 (3)	34 (4)	43 (4)
F4	3155 (3)	2608 (5)	2490 (2)	103 (3)	117 (4)	101 (3)	37 (3)	-15 (3)	-21 (3)
F5	-203 (4)	2925 (7)	3967 (6)	116 (5)	140 (6)	452 (14)	-19 (4)	25 (7)	78 (8)
F6	471 (3)	1287 (5)	4428 (3)	147 (4)	85 (3)	142 (4)	-1 (3)	45 (4)	15 (3)
F7	1061 (3)	3182 (5)	4591 (3)	107 (4)	158 (5)	158 (5)	-59 (4)	7 (3)	-51 (4)
F8A	296 (8)	2600 (11)	3442 (5)	205 (14)	148 (10)	46 (6)	-58 (10)	13 (8)	4 (6)
F8B	960 (8)	2029 (16)	3690 (7)	152 (11)	336 (20)	124 (10)	-18 (12)	97 (9)	-31 (12)
N1	6808 (3)	3015 (5)	3516 (3)	63 (3)	54 (4)	54 (3)	-1 (3)	23 (3)	-2 (3)
N16	6321 (3)	-39 (5)	3734 (3)	57 (3)	53 (4)	78 (4)	-8 (3)	40 (3)	-8 (3)
N8	7728 (3)	813 (5)	3639 (2)	43 (3)	55 (3)	44 (3)	-4 (3)	20 (3)	5 (3)
N16'	9140 (3)	2526 (5)	1556 (2)	44 (3)	62 (4)	46 (3)	-8 (3)	19 (3)	1 (3)
N1'	7137 (3)	2159 (5)	866 (2)	44 (3)	54 (4)	45 (3)	3 (3)	14 (3)	2 (3)
N8'	8276 (3)	730 (4)	1979 (2)	44 (3)	54 (3)	42 (3)	3 (3)	18 (3)	2 (3)
C17	5776 (4)	1289 (7)	2047 (4)	66 (5)	75 (5)	66 (5)	12 (4)	9 (4)	-3 (5)
C6	7581 (4)	3044 (6)	4018 (3)	59 (4)	69 (5)	47 (4)	-7 (4)	30 (4)	-3 (4)
C5	7967 (4)	4201 (7)	4325 (4)	73 (5)	82 (6)	72 (5)	-17 (4)	40 (4)	-22 (5)
C4	7542 (5)	5315 (7)	4115 (4)	108 (7)	71 (6)	96 (6)	-23 (5)	64 (5)	-30 (5)
C3	6756 (5)	5299 (7)	3602 (4)	107 (6)	63 (5)	84 (6)	9 (5)	61 (5)	6 (5)
C2	6407 (4)	4138 (7)	3320 (4)	72 (5)	60 (5)	73 (5)	5 (4)	28 (4)	-5 (4)
C11	7005 (4)	-660 (6)	4159 (3)	81 (5)	41 (4)	66 (5)	2 (4)	46 (4)	5 (4)
C12	7049 (5)	-1400 (7)	4755 (4)	126 (7)	55 (5)	97 (6)	12 (5)	72 (5)	6 (4)
C13	6346 (6)	-1533 (7)	4905 (5)	189 (10)	49 (5)	141 (8)	-6 (6)	123 (8)	7 (5)
C14	5651 (6)	-956 (8)	4449 (5)	138 (8)	63 (6)	170 (9)	-27 (5)	119 (8)	-21 (6)
C15	5637 (4)	-208 (7)	3869 (4)	77 (5)	62 (5)	117 (6)	-18 (4)	54 (5)	-29 (5)
C7	7977 (4)	1766 (7)	4251 (3)	53 (4)	84 (5)	45 (4)	-11 (4)	17 (3)	-2 (4)
C10	7719 (4)	-495 (6)	3935 (3)	63 (4)	65 (5)	58 (4)	11 (4)	27 (4)	12 (4)
C9	8280 (3)	914 (6)	3246 (3)	49 (4)	71 (5)	54 (4)	-3 (3)	17 (3)	3 (4)
C17'	7984 (4)	4132 (7)	2268 (4)	72 (5)	77 (6)	91 (6)	7 (4)	26 (4)	-28 (5)
C11'	9486 (3)	1372 (6)	1741 (3)	38 (4)	76 (5)	51 (4)	2 (4)	20 (3)	5 (4)
C12'	10103 (4)	979 (7)	1525 (4)	64 (5)	88 (6)	93 (6)	-1 (4)	40 (4)	-2 (5)
C13'	10375 (4)	1827 (9)	1132 (5)	69 (5)	141 (8)	113 (7)	-19 (5)	63 (5)	-12 (6)
C14'	10044 (5)	3015 (8)	965 (4)	90 (6)	104 (7)	80 (6)	-42 (5)	41 (5)	-3 (5)
C15'	9423 (4)	3332 (6)	1186 (3)	63 (5)	78 (5)	51 (4)	-21 (4)	17 (4)	-1 (4)
C6'	7083 (3)	886 (6)	780 (3)	51 (4)	52 (4)	39 (4)	-4 (4)	21 (3)	-1 (3)
C5'	6405 (4)	313 (6)	262 (3)	76 (5)	52 (5)	61 (5)	-8 (4)	31 (4)	-5 (4)
C4'	5767 (4)	1070 (7)	-202 (3)	55 (4)	86 (6)	50 (4)	-12 (4)	8 (4)	-7 (4)
C3'	5825 (4)	2353 (7)	-122 (3)	55 (4)	78 (5)	55 (4)	7 (4)	18 (4)	15 (4)

Table III (Continued)

	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
C2'	6518 (4)	2875 (6)	417 (4)	61 (4)	49 (4)	71 (5)	-3 (4)	25 (4)	6 (4)
C10'	9167 (3)	539 (6)	2192 (3)	49 (4)	69 (5)	59 (4)	16 (4)	20 (3)	8 (4)
C7'	7827 (3)	129 (6)	1242 (3)	55 (4)	50 (4)	54 (4)	2 (3)	23 (3)	-2 (3)
C9'	7987 (3)	166 (6)	2526 (3)	51 (4)	61 (4)	58 (4)	-5 (3)	26 (3)	0 (4)

<sup>a</sup> Fractional coordinates have been multiplied by 10<sup>5</sup> for the copper atoms and by 10<sup>4</sup> for all other atoms.  $U_{ij}$  has been multiplied by 10<sup>4</sup> for the copper atoms and by 10<sup>3</sup> for all other atoms. <sup>b</sup> The form of the thermal ellipsoid is  $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$  for the anisotropic thermal parameters.

Table IV. Hydrogen Atomic Parameters for Cu<sub>2</sub>(TPEN)(BF<sub>4</sub>)<sub>2</sub> (1) and Cu<sub>2</sub>(TPEN)(CO)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> (2)<sup>a</sup>

	x <sup>b</sup>	y	z	B, Å <sup>2</sup>
Cu <sub>2</sub> (TPEN)(BF <sub>4</sub> ) <sub>2</sub>				
H2	170	-103	116	7.8
H3	348	-120	112	7.8
H4	461	-6	146	8.2
H5	397	123	181	8.0
H7A	165	192	127	7.2
H7B	250	203	222	7.2
H9A	16	237	157	8.0
H9B	89	281	246	8.0
H10A	110	160	382	7.3
H10B	223	176	362	7.3
H12	346	64	397	6.6
H13	381	-80	423	7.4
H14	235	-172	417	6.7
H15	66	-117	377	7.1
Cu <sub>2</sub> (TPEN)(CO) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub>				
H2	588	414	299	6.1
H3	648	605	345	6.8
H4	778	607	431	7.0
H5	848	422	466	6.4
H7A	785	146	462	5.5
H7B	853	187	443	5.5
H9A	833	175	315	5.4
H9B	878	62	354	5.4
H10A	769	-109	359	5.6
H10B	819	-63	433	5.6
H12	753	-179	505	7.7
H13	635	-198	530	8.6
H14	519	-108	453	8.1
H15	516	17	357	7.3
H2'	655	374	47	5.8
H3'	542	286	-41	6.0
H4'	532	70	-55	6.3
H5'	638	-56	22	5.8
H7A'	817	6	100	5.2
H7B'	767	-68	131	5.2
H9A'	744	14	233	5.1
H9B'	817	-65	262	5.1
H10A'	943	72	268	5.6
H10B'	927	-30	213	5.6
H12'	1032	18	164	7.3
H13'	1077	159	98	8.4
H14'	1023	358	72	7.6
H15'	920	413	108	6.0

<sup>a</sup> Each atom is given the same number as the carbon to which it is bound. <sup>b</sup> Fractional coordinates have been multiplied by 10<sup>3</sup>.

**Cu<sub>2</sub>(TPEN)(BF<sub>4</sub>)<sub>2</sub> (1).** The following was performed under helium in a Vacuum Atmospheres Dri-Lab inert-atmosphere chamber. Cu(CH<sub>3</sub>CN)<sub>4</sub>BF<sub>4</sub> (0.315 g, 1 mmol) was added to a solution of TPEN (0.21 g, 0.5 mmol) in 25 mL of acetonitrile. After the mixture was stirred for 10 min at ambient temperature, the solvent was removed under vacuum. Addition of methanol (25 mL) to the resulting orange oil yielded a slightly slightly yellow-green crystalline product. The product was collected by vacuum filtration, washed with methanol, and dried for several hours in vacuo. Anal. (C<sub>26</sub>H<sub>28</sub>N<sub>6</sub>Cu<sub>2</sub>B<sub>2</sub>F<sub>8</sub>) C, H, N.

Table V. Interatomic Distances (Å) for Cu<sub>2</sub>(TPEN)(BF<sub>4</sub>)<sub>2</sub> (1) and Cu<sub>2</sub>(TPEN)(CO)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> (2)

Cu <sub>2</sub> (TPEN)(BF <sub>4</sub> ) <sub>2</sub> <sup>a</sup>			
Cu-Cu'	2.779 (2)	C11-C12	1.383 (12)
Cu-N1	1.936 (7)	C11-N16	1.339 (11)
Cu-N8	2.295 (7)	C12-C13	1.384 (13)
Cu-N16'	1.890 (8)	C13-C14	1.399 (14)
N1-C2	1.346 (12)	C14-C15	1.386 (14)
N1-C6	1.355 (12)	C15-N16	1.330 (12)
C2-C3	1.398 (15)	BA-F1A	1.284
C3-C4	1.356 (16)	BA-F2A	1.411
C4-C5	1.353 (16)	BA-F3A	1.398
C5-C6	1.402 (15)	BA-F4A	1.406
C6-C7	1.513 (14)	BB-F1B	1.36
C7-N8	1.490 (12)	BB-F2B	1.20
N8-C9	1.501 (11)	BB-F3B	1.24
N8-C10	1.496 (11)	BB-F4B	1.23
C9-C9'	1.521 (13)	Cu-N16	2.827 (8)
C10-C11	1.495 (13)		
Cu <sub>2</sub> (TPEN)(CO) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub>			
Cu-N1	2.042 (5)	Cu'-N1'	2.036 (5)
Cu-N16	2.030 (5)	Cu'-N16'	2.032 (5)
Cu-N8	2.169 (5)	Cu'-N8'	2.160 (5)
Cu-C17	1.809 (7)	Cu'-C17'	1.781 (7)
N1-C6	1.341 (8)	N1'-C6'	1.330 (8)
N1-C2	1.341 (9)	N1'-C2'	1.334 (9)
N16-C11	1.340 (8)	N16'-C11'	1.329 (8)
N16-C15	1.346 (9)	N16'-C15'	1.326 (8)
N8-C7	1.482 (8)	N8'-C7'	1.489 (8)
N8-C10	1.479 (8)	N8'-C10'	1.481 (8)
N8-C9	1.465 (8)	N8'-C9'	1.476 (8)
C17-O18	1.100 (9)	C17'-O18'	1.110 (10)
C6-C5	1.396 (9)	C6'-C5'	1.372 (9)
C6-C7	1.487 (9)	C6'-C7'	1.499 (9)
C5-C4	1.353 (11)	C5'-C4'	1.387 (9)
C4-C3	1.366 (11)	C4'-C3'	1.340 (10)
C3-C2	1.369 (11)	C3'-C2'	1.383 (10)
C11-C12	1.375 (9)	C11'-C12'	1.378 (9)
C11-C10	1.500 (9)	C11'-C10'	1.494 (8)
C12-C13	1.391 (11)	C12'-C13'	1.374 (11)
C13-C14	1.350 (12)	C13'-C14'	1.350 (11)
C14-C15	1.369 (11)	C14'-C15'	1.368 (10)
C9-C9'	1.515 (9)	B2-F5	1.369 (14)
B1-F1	1.333 (13)	B2-F6	1.327 (12)
B1-F2	1.347 (13)	B2-F7	1.301 (12)
B1-F3	1.362 (13)	B2-F8A	1.247 (16)
B1-F4	1.340 (14)	B2-F8B	1.356 (19)
Cu-Cu'	4.764 (1)		

<sup>a</sup> For compound 1 only, primes are used to designate atoms operated upon by the twofold axis (i.e.,  $\bar{x}$ ,  $y$ ,  $1/2 - z$ ).

**Cu<sub>2</sub>(TPEN)(CO)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> (2).** A suspension of 1 (ca. 100 mg) in 20 mL of methanol (under helium) was placed in an Erlenmeyer flask and covered with a rubber septum. Purging the system with CO caused dissolution of the solid. Evaporation of the solvent with a slow stream of CO yielded off-white crystals of 2. Anal. (C<sub>28</sub>H<sub>28</sub>N<sub>6</sub>O<sub>2</sub>Cu<sub>2</sub>B<sub>2</sub>F<sub>8</sub>) C, H, N; Cu: calcd, 16.3; found, 16.8.

**Physical Measurements.** Sample preparation for physical studies on the air-sensitive materials was accomplished in a Vacuum Atmospheres Dri-Lab inert-atmosphere chamber, under a helium atmosphere. Helium-saturated spectroquality solvents were used for solution studies.

Electronic spectra were recorded on a Cary 14 spectrophotometer. Solid-state spectra were obtained from Nujol mulls on filter paper (under He) against a Nujol-saturated filter paper as a blank.

**Table VI.** Interatomic Angles (Deg) for Cu<sub>2</sub>(TPEN)(BF<sub>4</sub>)<sub>2</sub> (1) and Cu<sub>2</sub>(TPEN)(CO)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> (2)

Cu <sub>2</sub> (TPEN)(BF <sub>4</sub> ) <sub>2</sub>			
N1-Cu-Cu'	129.6 (2)	C11-C10-N8	111.0 (7)
N8-Cu-Cu'	77.7 (2)	C12-C11-C10	121.9 (8)
N16'-Cu-Cu'	71.7 (2)	N16-C11-C10	115.5 (8)
N8-Cu-N1	82.0 (3)	N16-C11-C12	122.5 (8)
N16'-Cu-N1	146.8 (3)	C13-C12-C11	120.2 (8)
N16'-Cu-N8	130.8 (3)	C14-C13-C12	117.3 (9)
C2-N1-Cu	125.3 (3)	C15-C14-C13	118.6 (9)
C6-N1-Cu	116.9 (6)	N16-C15-C14	123.9 (9)
C6-N1-C2	117.2 (8)	C11-N16-Cu'	124.1 (6)
C3-C2-N1	122.7 (9)	C15-N16-Cu'	118.4 (6)
C4-C3-C2	119.2 (10)	C15-N16-C11	117.5 (8)
C5-C4-C3	119.5 (11)	F2A-BA-F1A	104.9
C6-C5-C4	120.0 (10)	F3A-BA-F1A	110.0
C5-C6-N1	121.5 (9)	F4A-BA-F1A	108.4
C7-C6-N1	114.9 (8)	F3A-BA-F2A	111.6
C7-C6-C5	123.5 (9)	F4A-BA-F2A	113.7
N8-C7-C6	112.0 (8)	F4A-BA-F3A	108.1
C7-N8-Cu	97.9 (5)	F2B-BB-F1B	110.9
C9-N8-Cu	114.8 (5)	F3B-BB-F1B	110.8
C10-N8-Cu	113.6 (5)	F4B-BB-F1B	113.2
C9-N8-C7	106.7 (7)	F3B-BB-F2B	109.1
C10-N8-C7	110.5 (7)	F4B-BB-F2B	105.0
C10-N8-C9	112.1 (6)	F4B-BB-F3B	107.6
C9'-C9-N8	114.3 (7)		
Cu <sub>2</sub> (TPEN)(CO) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub>			
N16-Cu-N1	110.9 (4)	N16'-Cu'-N1'	108.1 (4)
N8-Cu-N1	81.9 (4)	N8'-Cu'-N1'	82.2 (4)
C17-Cu-N1	116.7 (4)	C17'-Cu'-N1'	118.7 (4)
N8-Cu-N16	80.6 (4)	N8'-Cu'-N16'	81.4 (4)
C17-Cu-N16	122.1 (4)	C17'-Cu'-N16'	121.8 (4)
C17-Cu-N8	135.6 (4)	C17'-Cu'-N8'	134.9 (4)
C6-N1-Cu	114.4 (5)	C6'-N1'-Cu'	114.6 (5)
C2-N1-Cu	126.9 (5)	C2'-N1'-Cu'	126.9 (5)
C2-N1-C6	117.9 (6)	C2'-N1'-C6	114.4 (5)
C11-N16-Cu	115.8 (5)	C11'-N16'-Cu'	126.0 (5)
C15-N16-Cu	125.0 (5)	C15'-C16'-Cu'	126.0 (5)
C15-N16-C11	118.7 (6)	C15'-C16'-C11'	119.1 (6)
C7-N8-Cu	103.3 (5)	C7'-N8'-Cu'	104.0 (5)
C10-N8-Cu	104.7 (5)	C10'-N8'-Cu'	103.6 (5)
C9-N8-Cu	116.8 (5)	C9'-N8'-Cu'	118.1 (5)
C10-N8-C7	109.9 (6)	C10'-N8'-C7'	109.3 (6)
C9-N8-C7	109.1 (6)	C9'-N8'-C7'	109.5 (6)
C9-N8-C10	112.5 (6)	C9'-N8'-C10'	111.9 (6)
O18-C17-Cu	174.7 (6)	O18'-C17'-Cu'	176.0 (6)
C5-C6-N1	121.7 (6)	C5'-C6'-N1'	121.6 (6)
C7-C6-N1	115.6 (6)	C7'-C6'-N1'	116.1 (6)
C7-C6-C5	122.7 (6)	C7'-C6'-C5'	122.2 (6)
C6-C5-C4	118.8 (7)	C6'-C5'-C4'	119.8 (6)
C3-C4-C5	120.1 (8)	C3'-C4'-C5'	118.7 (7)
C2-C3-C4	118.7 (8)	C2'-C3'-C4'	118.9 (7)
C3-C2-N1	122.8 (7)	C3'-C2'-N1'	123.1 (7)
C12-C11-N16	122.5 (6)	C12'-C11'-N16'	121.3 (6)
C10-C11-N16	115.1 (6)	C10'-C11'-N16'	116.3 (6)
C10-C11-C12	122.4 (6)	C10'-C11'-C12'	122.4 (6)
C13-C12-C11	118.3 (7)	C13'-C12'-C11'	118.3 (7)
C14-C13-C12	118.5 (8)	C14'-C13'-C12'	120.5 (8)
C15-C14-C13	121.3 (8)	C15'-C14'-C13'	118.0 (7)
C14-C15-N16	120.6 (7)	C14'-C15'-N16'	122.8 (6)
C6-C7-N8	112.9 (6)	C6'-C7'-N8'	112.4 (6)
C11-C10-N8	110.9 (6)	C11'-C10'-N8'	111.1 (6)
C9'-C9-N8	113.4 (6)	C9-C9'-N8'	112.6 (6)
F2-B1-F1	111.5 (9)	F6-B2-F5	100.4 (9)
F3-B1-F1	105.9 (9)	F7-B2-F5	104.4 (9)
F4-B1-F1	110.5 (9)	F8A-B2-F5	77.0 (11)
F3-B1-F2	107.7 (9)	F8B-B2-F5	133.2 (12)
F4-B1-F1	110.3 (9)	F8B-B2-F6	102.7 (11)
F4-B1-F3	110.9 (9)	F8A-B2-F7	121.0 (10)
F7-B2-F6	112.8 (10)	F8B-B2-F7	103.2 (11)
F8A-B2-F6	125.1 (10)	F8B-B2-F8A	56.5 (12)

<sup>a</sup> See footnote a for Table V.

Infrared spectra were recorded on a Beckman IR-12 infrared spectrophotometer. Solid-state spectra were obtained from Nujol mulls pressed between KBr plates. Solution spectra were obtained with use of calcium fluoride solution cells (path length of 1 mm).

Proton magnetic resonance spectra were recorded on a Varian EM390 spectrophotometer at 90 MHz (34 °C). The solvent utilized was CD<sub>3</sub>CN containing Me<sub>4</sub>Si as the reference.

Elemental analyses were performed by the Caltech Microanalytical Laboratory.

**Crystallographic Characterization of Cu<sub>2</sub>(TPEN)(BF<sub>4</sub>)<sub>2</sub> (1).** Yellow needles were grown by slow evaporation under helium of a solution of **1** in acetonitrile/bis(2-methoxyethyl) ether (ca. 1:1). Preliminary Weissenberg and precession photographs showed the crystals to be monoclinic with the *c* axis parallel to the needle axis. Systematic absence of the reflections *hkl* with *h* + *k* odd and *h0l* with *l* odd indicated the space group to be *Cc* (No. 9) or *C2/c* (No. 15); the latter was shown to be correct by satisfactory solution and refinement of the structure.

A crystal of dimensions 0.31 × 0.12 × 0.07 mm was cut from a longer needle and mounted on a Syntex P2<sub>1</sub> four-circle diffractometer equipped with graphite-monochromatized Mo K $\alpha$  radiation. Cell parameters (Table II) were determined by a least-squares fit to 15 automatically centered reflections with 18° < 2 $\theta$  < 25°. Intensity data were collected for the hemisphere  $\pm h, \pm k, l$  (excluding reflections with *k* + *l* odd) with use of  $\theta$ -2 $\theta$  scans. The maximum 2 $\theta$  value was 45° for the quadrant with *k* ≥ 0 and 25° for *k* ≤ 0. The scan range extended from 1° below the Mo K $\alpha_1$  2 $\theta$  value to 1° above the Mo K $\alpha_2$  value, and the scan rate was 1°/min, with the total background counting time equal to the total scan time. Three check reflections were measured after every 60 reflections to monitor the crystal and instrument stability. These showed no systematic variations throughout the course of data collection.

The data were corrected for Lorentz and polarization effects and for absorption by the method of Gaussian quadrature.<sup>16</sup> Standard deviations of intensities were calculated with use of the formula

$$\sigma^2(F_o^2) = [S + (B_1 + B_2) + (dS)^2]/(Lp)^2$$

where *S*, *B*<sub>1</sub>, and *B*<sub>2</sub> are the scan and two background counts and *d* was taken as 0.02.<sup>17</sup> After symmetry-extinct reflections were deleted, data from the two quadrants were averaged. There resulted 1941 unique data, with 1598 of these greater than zero.

With the exception of C. K. Johnson's ORTEP program, all computer programs were from the CRYM system. All scattering factors (Cu<sup>+</sup>, F, N, C, B) with the exception of those for hydrogen<sup>18</sup> were taken from ref 19 as was the real part of the anomalous dispersion correction for copper. The function minimized in the least-squares refinement was  $\sum w(F_o^2 - F_c^2)^2$ , where the weight  $w = 1/\sigma^2(F_o^2)$ .

The position of the copper atom was determined by means of a three-dimensional Patterson synthesis, and a subsequent electron density map revealed the positions of most of the carbon and nitrogen atoms. A cycle of least-squares, followed by another Fourier map, gave the positions of the remaining nonhydrogen atoms. Full-matrix least-squares refinement including all of these atoms with isotropic temperature factors led to  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.111$  for those reflections with  $F_o^2 > 3\sigma$ . Use of anisotropic temperature factors lowered *R* to 0.067. Hydrogen atom positions were calculated with the assumption of a carbon-hydrogen distance of 0.97 Å. All of these corresponded to regions of positive electron density in a difference Fourier map. Hydrogen atoms were included in the least-squares with the isotropic temperature factor for each fixed at 1.0 Å<sup>2</sup> greater than that previously determined for the bound carbon atom. The hydrogen positional parameters were not refined but were recalculated periodically.

The large and highly anisotropic temperature factors, which had been determined at this point for the fluorine and boron atoms, indicated a probability of disordering of the BF<sub>4</sub><sup>-</sup> anion. A detailed Fourier map of the anion showed that the fluorine atoms occupied two different sets of positions, although one of these sets had a much lower occupancy than the other. Consequently, two partial BF<sub>4</sub><sup>-</sup> groups were included in the least-squares along with a single population factor. The fluorine atoms in the more and less heavily occupied positions were refined with anisotropic and isotropic temperature factors, re-

(16) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180-182.

(17) Peterson, S. W.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 70-76.

(18) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175-3187.

(19) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III.

spectively. The boron atom for each of these  $\text{BF}_4^-$  groups was placed at coordinates calculated by averaging the corresponding fluorine coordinates. These coordinates were not refined but were recalculated periodically (final boron-boron separation = 0.50 Å). The isotropic temperature factors for the boron atoms were refined. The populations for the groups refined to final values of 0.71 and 0.29.

The final refinement of the structure was done by block-diagonal least-squares with two matrices. All nonhydrogen positional parameters were included in one matrix; the second contained all nonhydrogen thermal parameters, the  $\text{BF}_4^-$  population factor, and the scale factor. No reflections were omitted from this refinement. The final  $R$  was 0.051 for the 665 reflections with  $F_o^2 > 3\sigma$  and 0.143 for all data. The goodness of fit  $[\sum w(F_o^2 - F_c^2)^2 / (m - s)]^{1/2}$  was 1.19, where  $m = 1941$  is the number of observations and  $s = 209$  is the number of parameters. Features on a final difference map were between  $-1.4 \text{ e}/\text{Å}^3$  (at the position of Cu) and  $1.2 \text{ e}/\text{Å}^3$  (near F4A). Final atomic parameters are given in Tables III and IV.

**Crystallographic Characterization of  $\text{Cu}_2(\text{TPEN})(\text{CO})_2(\text{BF}_4)_2$  (2).** An approximately cubic crystal, 0.2 mm on an edge, was sealed in epoxy to prevent decomposition and was used for all X-ray diffraction measurements. Preliminary oscillation and Weissenberg photographs showed Laue symmetry  $2/m$  with systematic absences  $h0l$  with  $l$  odd and  $0k0$  with  $k$  odd, indicating the monoclinic space group  $P2_1/c$ ; the crystal was then transferred to a Syntex  $P2_1$  diffractometer operating with Ni-filtered  $\text{Cu K}\alpha$  radiation. Unit cell dimensions were obtained by centering 15 well-scattered reflections with  $2\theta$  values ranging from 23 to 48°. Intensities were measured with use of a  $\theta$ - $2\theta$  scan at a rate of 2°/min with an equal amount of time spent on backgrounds; three check reflections, monitored every 100 measurements, showed no intensity decay or abnormal fluctuations. All reflections out to  $2\theta = 100^\circ$  were measured in two different quadrants ( $\pm h, k, l$  and  $\pm h, -k, -l$ ) and were averaged to yield 3558 net intensities, of which 2998 were greater than zero.

The initial attempt at solving the structure was by manual application of direct methods based on 95 reflections with  $|E|$  greater than 1.85, three origin-fixing signs, and two symbolic signs. The resulting  $E$  map was not structurally reasonable because, as it turned out, one of the early sign entries was reversed. A three-dimensional

Patterson map was then calculated and quickly led to the positions of the Cu atoms. The C, N, O, B, and F atoms were recovered from  $F_o$  and difference maps; the positions of the hydrogen atoms were calculated with use of a C-H bond length of 0.9 Å. In the least-squares refinement the same quantity was minimized as in the preceding structure, with weights calculated in the same manner.

A late difference map indicated rather severe disorder for one of the  $\text{BF}_4^-$  groups: while three of the fluorine atoms could be adequately represented by large, anisotropic  $B$ 's, the fourth could not and accordingly was split into two half-occupied sites separated by about 1.2 Å.

In the final least-squares cycles, three matrices were collected, each of order between 140 and 150: the coordinates of the 49 nonhydrogen atoms in one, anisotropic  $B$ 's for half the cation and one of the  $\text{BF}_4^-$  groups in a second, and anisotropic  $B$ 's of the remaining atoms, a scale factor, and an extinction parameter in the third. The final value of the goodness of fit was 1.87 for the 3558 measured reflections; the  $R$  factors were 0.062 for the 2998 reflections with net intensity greater than zero and 0.042 for the 2271 reflections with intensities greater than 3 esd's above background. Features on a difference map were between  $-0.8$  and  $0.6 \text{ e}/\text{Å}^3$ , in generally uninteresting places.

All calculations were carried out on the CRYM system of programs. Final atomic parameters are given in Tables III and IV, on the basis of the numbering scheme shown in Figure 4.

**Acknowledgment.** We appreciate helpful discussions with Grant A. Mauk and financial assistance from the National Institutes of Health (Grant No. PHS AM18319), the International Copper Research Association, and a Sloan Fellowship (to R.R.G.).

**Registry No.** 1, 79483-34-4; 2, 79483-36-6;  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ , 15418-29-8.

**Supplementary Material Available:** Listings of the observed and calculated structure factors for  $\text{Cu}_2(\text{TPEN})(\text{BF}_4)_2$  and  $\text{Cu}_2(\text{TPEN})(\text{CO})_2(\text{BF}_4)_2$  (22 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,  
University of New Mexico, Albuquerque, New Mexico 87131

## Synthesis and Crystal and Molecular Structure of a [Diethyl (*N,N*-diethylcarbamyl)methylenephosphonate]thorium Nitrate Complex

S. M. BOWEN, E. N. DUESLER, and R. T. PAINE\*

Received April 16, 1981

[Diethyl (*N,N*-diethylcarbamyl)methylenephosphonate]thorium(IV) nitrate,  $\text{Th}[(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{N}(\text{C}_2\text{H}_5)_2]_2(\text{NO}_3)_4$  (1), has been prepared from the combination of an acidic solution of  $\text{Th}(\text{NO}_3)_4$  and a benzene solution of the carbamyl phosphonate ligand. The resulting complex has been characterized by infrared and  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopies. A single-crystal X-ray analysis of 1 has been completed, and the complex was found to crystallize in the monoclinic space group  $C2/c$  with  $a = 20.754$  (6) Å,  $b = 8.470$  (1) Å,  $c = 21.183$  (5) Å,  $\beta = 101.69$  (2)°,  $Z = 4$ ,  $V = 3646.6$  Å<sup>3</sup>, and  $\rho_{\text{calc}} = 1.79 \text{ g cm}^{-3}$ . The structure was solved by standard heavy-atom techniques. Full-matrix least-squares refinement of the structure has led to final discrepancy indices of  $R_F = 4.0\%$  and  $R_{wF} = 5.0\%$  on the basis of 4385 independent reflections. The crystal contains monomeric units of 1 that have crystallographic  $C_2$  symmetry. The thorium atom is bonded to both carbonyl and phosphoryl oxygen atoms of two carbamyl phosphonate ligands and two oxygen atoms of each of four nitrate groups. The resulting coordination number for the thorium atom is 12. Several important bond distances include Th-O(carbonyl) 2.453 (4) Å, Th-O(phosphoryl) 2.482 (4) Å, and Th-O(nitrate) 2.638 (3) Å (average).

### Introduction

Siddall and co-workers<sup>1-3</sup> and more recently Petrzilova<sup>4</sup> and Schulz and McIsaac<sup>5</sup> have studied the extraction chemistry of carbamylmethylenephosphonate (CMP) ligands with a

number of lanthanide and actinide ions found in liquid, acidic, radioactive waste. Primarily on the basis of equilibrium distribution measurements, it has been concluded that trivalent lanthanide and actinide ions form tris-chelate complexes,  $\text{M}(\text{CMP})_3^{3+}$ , in which the metal ion is bonded to the CMP ligands in a bidentate coordination mode through the carbonyl and phosphoryl oxygen atoms.<sup>1-5</sup> Some limited infrared spectroscopic data appear to support the structural assumption,<sup>3,6</sup> however, unambiguous stoichiometry and structure

- (1) Siddall, T. H. *J. Inorg. Nucl. Chem.* **1963**, *25*, 883.
- (2) Siddall, T. H. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1991.
- (3) Stewart, W. E.; Siddall, T. H. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3599.
- (4) Petrzilova, H.; Binka, J.; Kuca, L. *J. Radioanal. Chem.* **1979**, *51*, 107.
- (5) Schulz, W. W.; McIsaac, L. D. "Transplutonium Elements"; Müller, W., Lindner, R., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; p 433.

- (6) Stewart, W. E.; Siddall, T. H. *J. Inorg. Nucl. Chem.* **1968**, *30*, 3281.