of Health under Grant No. 5-R01-GM32296-03 for support of this research.

Registry No. $[(bpy)_2Ru(H_2O)]_2O^{4+}$, 56110-87-3; $[(bpy)_2Ru(H_2O)]_2O^{5+}$, 96364-22-6; $(bpy)_2(H_2O)Ru^{III}ORu^{IV}(OH)(bpy)_2{}^{4+}$, 86045-59-2; *cis*-$(bpy)_2Ru(H_2O)^{2+}$, 72174-10-8; *cis*-$(bpy)_2Ru^{III}(H_2O)(OH)^{2+}$, 85027-43-6; $(bpy)_2(H_2O)RuORu(bpy)_2ORu(H_2O)(bpy)_2{}^{4+}$, 101695-59-4; $[(bpy)_2Os(H_2O)_2](ClO_4)_2$, 84988-26-1; *trans*-$(bpy)_2Ru(H_2O)^{2+}$, 72174-09-5; $[(bpy)_2Os(H_2O)]_2O^{4+}$, 99626-17-2; $(bpy)_2Ru(OH_2)ORu(OH)(bpy)_2{}^{3+}$, 100570-91-0; $[[(bpy)_2Os(H_2O)]_2O](ClO_4)_4$, 101695-60-7; $[[(bpy)_2Ru(H_2O)]_2O](ClO_4)_4$, 56110-88-4; $[(bpy)_2Ru(H_2O)_2](ClO_4)_2$, 16038-45-2; SnO_2, 18282-10-5; H_2O, 7732-18-5; Cl_2, 7782-50-5; Cl^-, 16887-00-6; C, 7440-44-0; O_2, 7782-44-7; Ru, 7440-18-8; Nafion, 39464-59-0.

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Crystal and Molecular Structure of $[Ag(tmbp)_2]BF_4$. Origin of Flattening Distortions in d^{10} Complexes of the Type $M(NN)_2{}^+$

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The crystal and molecular structure of colorless bis(4,4′,6,6′-tetramethyl-2,2′-bipyridyl)silver(I) tetrafluoroborate, $[Ag(tmbp)_2]BF_4$, has been determined and compared with those of Cu(I) complexes with analogous heteroaromatic, chelating ligands. The Cu(I) complexes are pseudotetrahedral, but they exhibit a characteristic flattening distortion, which results in a dihedral angle of 70–80° between the mean planes defined by the metal ion and each set of tmbp nitrogen atoms. The silver compound is found to be isomorphous and isostructural with $[Cu(tmpb)_2]ClO_4$. The dihedral angle defined above is 70.0 (1)° for the silver compound compared with 75.0° in the copper analogue. The fact that the dihedral angle in the Ag(I) complex is smaller than that in the Cu(I) complex tends to rule out the possibility that the flattening is due to an admixture of charge-transfer excited-state configurations in the ground state because the charge-transfer states are much less accessible in the Ag(I) system. The flattening is ascribed to a lattice effect that can be traced to stacking interactions involving the heteroaromatic ligands. The crystal system is orthorhombic, space group *Pbcn*, with $Z = 4$, $a = 16.737$ (2) Å, $b = 13.703$ (2) Å, $c = 11.916$ (2) Å, $V = 2733$ (1) Å^3, $R = 4.6\%$, and $R_w = 5.8\%$ for 1784 reflections.

Table I. Experimental Crystallographic Data for $[Ag(C_{14}N_2H_{16})_2]BF_4$

formula: $AgC_{28}N_4H_{32}BF_4$
mol. wt: 619.27
cryst dimens: 0.3 × 0.3 × 0.15 mm
cryst syst: orthorhombic
space group: Pbcn (No. 60)
cell dimens[a]: $a = 16.737$ (2) Å, $b = 13.703$ (2) Å, $c = 11.916$ (2) Å, $V = 2733$ (1) Å,^{3} $Z = 4$, D(calcd) = 1.505 g/cm^3
radiation: Cu Kα ($\lambda = 1.54184$ Å)
monochromator: graphite plate
θ range: 3–56°
max scan time: 60 s
scan angle: $1 + 0.14(\tan\theta)$
monitor reflecns: 3 every 2 h; 2% nonsystematic variations
h,k,l limits: 0–18,0–14,0–12
total no. of data: 1784
no. of unique data: 1784
no. of unique data with $F_o > 3\sigma(F_o)$: 1255
no. of variables: 221
μ(Cu Kα): 64.64 cm^{-1}
empirical abs cor: min trans, 79.7%; max, 99.9%; av, 94.5%
extinction: no cor necessary
$F(000)$: 1264
residuals: R, 0.046; R_w, 0.058
wt: $1/(\sigma(F_o))^2 = 4F_o^2/\sigma(F_o^2)$; $\sigma(F_o^2) = [(\sigma(F_o))^2 + 0.05F_o^2]^{1/2}$

[a] From least-squares refinement of the setting of 25 carefully centered reflections in the range $15° < \theta < 23°$.

Introduction

Heteroaromatic ligands such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline and their derivatives, generically labeled as NN ligands, have long been used as reagents for the spectrophotometric determination of iron and copper.[1,2] The method is based on the intense visible absorbances of the Fe(II) and Cu(I) complexes, which have low-lying metal-to-ligand charge-transfer (CT) excited states.[3,4] Formally, the excitation involves the transfer of an electron from the d shell of the metal center to π^* orbitals of the coordinated ligands. Recently, a number of groups have begun to explore the photochemistry and photophysics of the CT states.[5-10]

Because of the d^{10} configuration, it was originally assumed that the $Cu(NN)_2{}^+$ systems would have a pseudotetrahedral coordination geometry with a dihedral angle of 90° between the mean planes of the respective ligands.[2] However, several structures of $Cu(NN)_2{}^+$ systems have shown that the complexes are flattened with dihedral angles typically between 70 and 80°.[11-17] Drew and co-workers observed a similar geometry in bis(2,2′-bi-4,5-dihydrothiazine)copper(I) tetraphenylborate, and they suggested that an admixture of the CT configuration into the ground-state wave function could explain the flattening,[18] since Cu(II) character

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Table II. Positional Parameters, Equivalent Isotropic Temperature Factors, and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2
Ag	0	0.11700 (4)	1/4	3.37 (1)
N(1)	0.1128 (3)	0.0361 (3)	0.1860 (4)	2.7 (1)
N(2)	0.1113 (3)	0.1995 (3)	0.3174 (4)	2.4 (1)
C(1)	0.1127 (4)	−0.0476 (4)	0.1263 (6)	3.0 (1)
C(2)	0.1826 (5)	−0.0926 (5)	0.0931 (6)	3.6 (1)
C(3)	0.2557 (4)	−0.0540 (4)	0.1220 (6)	3.4 (1)
C(4)	0.2561 (4)	0.0316 (4)	0.1848 (6)	3.5 (2)
C(5)	0.1848 (1)	0.0751 (4)	0.2161 (5)	2.7 (1)
C(6)	0.1832 (4)	0.1671 (4)	0.2842 (5)	2.6 (1)
C(7)	0.2530 (4)	0.2150 (4)	0.3112 (6)	2.9 (1)
C(8)	0.2499 (4)	0.2996 (4)	0.3765 (6)	3.1 (1)
C(9)	0.1759 (4)	0.3320 (4)	0.4094 (6)	3.5 (1)
C(10)	0.1083 (4)	0.2828 (4)	0.3772 (6)	3.2 (1)
C(11)	0.0266 (4)	0.3191 (5)	0.4099 (6)	4.3 (2)
C(12)	0.3264 (5)	0.3518 (5)	0.4086 (7)	4.7 (2)
C(13)	0.3334 (5)	−0.0992 (5)	0.0884 (7)	5.0 (2)
C(14)	0.0335 (4)	−0.0891 (5)	0.0972 (7)	4.3 (2)
B	1/2	0.1144 (7)	1/2	4.9 (3)
F(1)	0.5541 (6)	0.1725 (7)	0.288 (1)	24.0 (4)
F(2)	0.473 (1)	0.0610 (7)	0.3202 (8)	28.7 (7)

[a] Equivalent isotropic thermal parameters are defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table III. Selected Bond Distances (Å) and Angles (deg)

Ag–N(1)	2.318 (5)	C(4)–C(5)	1.386 (9)
Ag–N(2)	2.323 (5)	C(5)–C(6)	1.499 (8)
N(1)–C(1)	1.349 (8)	C(6)–C(7)	1.379 (9)
N(1)–C(5)	1.367 (8)	C(7)–C(8)	1.398 (8)
N(2)–C(6)	1.341 (8)	C(8)–C(9)	1.373 (9)
N(2)–C(10)	1.347 (8)	C(8)–C(12)	1.516 (10)
C(1)–C(2)	1.381 (9)	C(9)–C(10)	1.371 (9)
C(1)–C(14)	1.483 (9)	C(10)–C(11)	1.506 (9)
C(2)–C(3)	1.376 (10)	B–F(1)	1.29 (1)
C(3)–C(4)	1.391 (9)	B–F(2)	1.20 (1)
C(3)–C(13)	1.494 (11)		
N(1)–Ag–N(2)	72.1 (2)	N(1)–Ag–N(2)^a	140.5 (2)
N(1)–Ag–N(1)^a	122.8 (2)	N(2)–Ag–N(2)^a	121.8 (2)

[a] Symmetry-related atoms at x, y, z and $-x$, y, $^1/_2$.

in the ground state would induce a pseudo-Jahn–Teller distortion. White and co-workers, who have examined a number of structures of Cu(NN)$_2^+$ complexes, have offered another interpretation.[17] They found that the dihedral angle varies with the anion and concluded that the flattening was imposed by some type of lattice interaction.

In an attempt to gain further insight into the basis of the distortion from tetrahedral symmetry, we have determined the crystal and molecular structure of [Ag(tmbp)$_2$]BF$_4$ where tmbp denotes 4,4′,6,6′-tetramethyl-2,2′-bipyridine. The CT state occurs at very high energy in the Ag(I) complex; therefore, the ground state can be expected to exhibit very little Ag(II) character. Significantly, we find that the complex exhibits an even smaller dihedral angle than was found in [Cu(tmbp)$_2$]ClO$_4$.

Experimental Section

AgBF$_4$ was purchased from Aldrich and used without purification. The tmbp was synthesized and purified by the method of Linnell.[19] The [Ag(tmbp)$_2$]BF$_4$ salt was synthesized by dissolving 1 mmol of AgBF$_4$ in 10 mL of methanol and then adding 30 mL of acetone containing 2 mmol of tmbp. The resulting solid was isolated by filtering, dissolved in acetone/methanol (3:1 by volume), and allowed to crystallize slowly in the dark. The colorless crystals had mixed habit but generally displayed $2/m$ symmetry with a tendency to favor rhombohedral plates. Spectra were measured with a Cary 17D spectrophotometer.

Crystallographic Data

Single-crystal data were collected at 22 °C by using techniques described previously.[14] Details of data collection and subsequent refinement are given in Table I. The orthorhombic symmetry of the crystal was verified by rapid collection of a spherical data set with $\theta < 25°$, which showed *mmm* symmetry.

The structure was solved by conventional Patterson and Fourier methods. Initial hydrogen atom positions were calculated. Final least-squares refinement cycles included all variable positions (including hydrogen) and anisotropic temperature factors for all atoms except the hydrogens, for which the isotropic temperature factors were fixed at 5.0 Å^2. The 1983 version of the SDP program package by Frenz was used for all calculations with least-squares minimization of $\sum = w(|F_o| - |F_c|)^2$. The final atomic coordinates and equivalent isotropic temperature factors for the heavy atoms may be found in Table II. Selected bond distances and angles are given in Table III. Thermal parameters, hydrogen parameters, other bond angles, equations of least-squares planes, and observed and calculated structure factors are available as supplementary material.

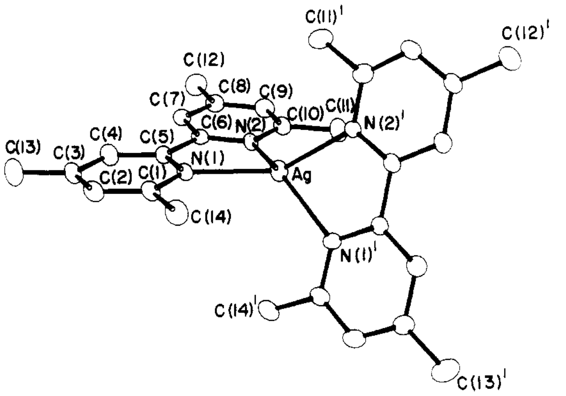

Figure 1. ORTEP drawing of Ag(tmbp)$_2^+$ showing 50% probability ellipsoids. The primed atomic centers are related to the unprimed counterparts by a 2-fold axis.

Results and Discussion

Crystals of [Ag(tmbp)$_2$]BF$_4$ are isomorphous and isostructural with [Cu(tmbp)$_2$]ClO$_4$.[15] The structure consists of discrete Ag(tmbp)$_2^+$ cations and uncoordinated BF$_4^-$ anions, both with crystallographic 2-fold symmetry. The BF$_4^-$ ions are almost disordered in pockets formed by methyl groups and two pairs of H(4) and H(7). The closest cation–anion approach is 2.66 (1) Å between F(1) and H(7) (between F(1) and C(7), 3.49 (1) Å). A view of the cation including the atom-numbering scheme is shown in Figure 1.

Coordination Geometry. Two symmetry-related bidentate tmbp ligands are coordinated to the Ag ion via the pyridine nitrogen atoms, which provide a distorted tetrahedral environment about Ag. The dimensions of the tmbp ligand are consistent with those observed in Cu(tmbp)$_2^+$ and other bipyridine derivatives. Each pyridine ring within a tmbp ligand is planar within experimental error, but there is a 4.0 (1)° twist about the 2,2′-carbon–carbon bond joining the rings. Such twists are observed in related bipyridine complexes with angles ranging from 0.1 to 11°.[20] The N(1)–N(2) distance (2.733 (6) Å) is larger than the corresponding distances of 2.65–2.67 Å in [Cu(dmbp)$_2$]BF$_4$,[14] [Cu(tmbp)$_2$]ClO$_4$,[15] and [Cu(tmbp)$_2$]Cl·2H$_2$O;[17] and the N(1)–Ag–N(2) bite angle of 72.1° (2) is smaller than the 80–82° bite angles found in these copper compounds, in accord with the longer Ag–N distances.

The two independent Ag–N distances are equivalent; Ag–N(av) = 2.320 Å. They are similar to Ag–N distances in other pseudotetrahedral complexes of Ag(I) with aromatic heterocyclic amine ligands: 2.373 (9) and 2.306 (6) Å in Ag(10-Me-isoalloxazine)$_2^+$,[21] 2.207 (3) Å in Ag(pic)$_2^-$ (pic = picolinate),[22] and 2.322 (3) Å

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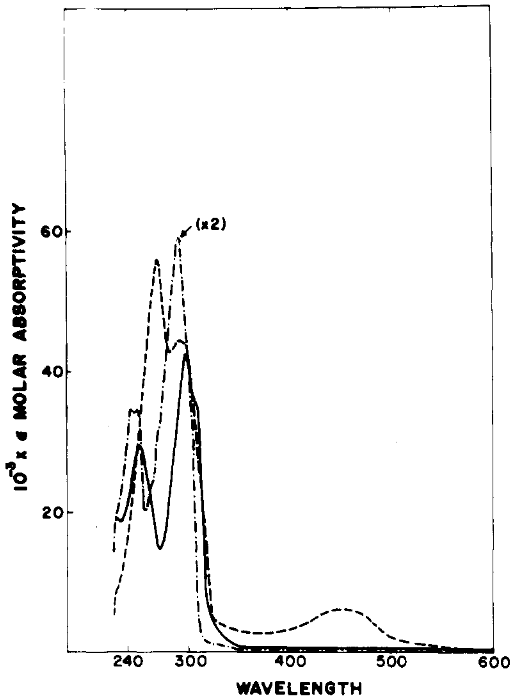

Figure 2. Absorption spectra of $Cu(tmbp)_2^+$ (--), $Ag(tmbp)_2^+$ (—), and tmbp (–•–) in CH_2Cl_2 at 22 °C.

in $Ag(py)_4^+$.[23,24] The 0.265-Å difference, Δ(M–L), in the average M–N distances in $Ag(tmbp)_2^+$ and $Cu(tmbp)_2^+$ is like those observed in $M(py)_4^+$, $M(NCC_2H_4CN)_2^+$, $M(NCCH_3)_4^+$, and $M_4I_4(pip)_4$ (pip = piperidine), which also contain equivalent Ag–N and Cu–N linkages.[23–30] In these compounds the Ag–N distances are on the average 0.28 Å longer than the corresponding Cu–N distances. A Δ(M–L) value of 0.40 Å is expected on the basis of the 4-coordinate ionic radii of Cu^+ and Ag^+,[31] but Δ(M–L) tends to decrease when covalent bonding forces are important.[24]

The dihedral angle between the planes defined by the Ag atom and each set of tmbp N atoms is 70.0 (1)° and is smaller than the corresponding angles of 75.0° in [$Cu(tmbp)_2$]ClO_4[15,32] and 79.0° in [$Cu(tmbp)_2$]$Cl\cdot 2H_2O$.[17] The dihedral angle in [$Cu(dmbp)_2$]BF_4 is 80.9°,[14] and in a series of analogous 2,9-dimethyl-1,10-phenanthroline complexes of Cu(I) these angles range from 72.4 to 85.4°,[17]

As noted above, it has been suggested that configuration interaction with $d^9\pi^{*1}$ excited states could explain the flattening observed in the Cu(I) systems.[18] In the Ag(I) complex, the CT excited states are much less accessible. As the CT absorption maximum occurs around 450 nm for $Cu(tmbp)_2^+$ (Figure 2) and the difference between the electron affinity of Ag^{2+} and Cu^{2+} is 1.2 eV, the corresponding CT band of the Ag(I) complex would be expected to occur in the UV region of the spectrum. However, the UV spectrum of $Ag(tmbp)_2^+$ is dominated by the π–π^* transitions of the ligand. The intraligand transitions, although they are slightly red-shifted as a result of complex formation, are easily identified by comparison with the spectrum of the free ligand. Small perturbations of these transitions are expected due to mixing with the metal orbitals and the fact that complexation induces a shift from the trans to the cis conformation about the C2–C2′ bond between pyridines. The lowest energy transition in the spectrum of $Ag(tmbp)_2^+$ occurs around 300 nm and appears as a shoulder in Figure 2. Even if this could be assigned as the CT transition, the energy separation from the ground state would be 50% greater for the Ag(I) system than it is for the analogous Cu(I) system. Since the extent of configuration interaction should vary inversely with the energy gap, no correlation between the flattening and the participation of the $d^9\pi^{*1}$ configuration is evident in these systems.

Table IV. C2–C2′ Bond Lengths in bpy Complexes

system	C2–C2′, Å	ref
$Fe(\eta^6\text{-}C_6H_5CH_3)(bpy)$	1.417 (3)	*a*
$Mo(O\text{-}i\text{-}Pr)_2(bpy)$	1.425 (4)	*b*
	1.424 (4)	
[$Co(bpy)_3$]$Cl\cdot H_2O$	1.40 (2)	*c*
	1.42 (3)	
	1.44 (3)	
cis-bpy	1.518	*d*
[$Cu(tmbp)_2$]ClO_4	1.480 (12)	*e*
[$Cu(tmbp)_2OClO_3$]ClO_4	1.478 (9)	*e*
	1.496 (9)	
[$Ag(tmbp)_2$]BF_4	1.499 (8)	*f*

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This conclusion is supported by the bond length comparisons presented in Table IV. The C2–C2′ bond lengths for the bpy moieties of the first three entries are all significantly shorter than that calculated for the free ligand, as expected for complexes of strongly reducing metal centers that delocalize electron density into the lowest energy π^* orbital.[33] In contrast, the C2–C2′ bond lengths of the Ag and Cu systems are little different from that of the free ligand. The difference is even less significant for the latter systems if the calculated value of the C2–C2′ bond length for *cis*-bpy overestimates the true bond length by 0.02 Å as is the case with the trans isomer.[34,35]

White and co-workers have argued that packing forces are important in determining the dihedral angle.[17] They have analyzed a series of analogous systems and have found that the dihedral angle varies significantly from structure to structure. In fact, the range of angles observed is wider than the deviation between the mean and 90°. If their explanation is correct, there should be a particular lattice interaction that is common to all the structures. The lattices are all ionic, but this in itself is not expected to cause flattening to occur. Each lattice also contains heteroaromatic ligands coordinated to the metal center, and in every case reported to date these ligands are involved in stacking interactions. We suggest that stacking forces promote the flattening distortions.

The energetics of such stacking interactions are complicated because multiple effects are involved. Thus, in a typical herringbone arrangement of planar aromatic systems, the packing energy is influenced in part by charge-transfer forces associated with the face-to-face contacts[36] and in part by static Coulombic forces, because the hydrogen atoms in aromatic hydrocarbons are positively charged with respect to the C atoms.[37] The resulting charge interactions are believed to help stabilize the slipped, approximately parallel geometries of stacked ring systems such as observed in the benzene dimer, trimer, and higher oligomers,[38]

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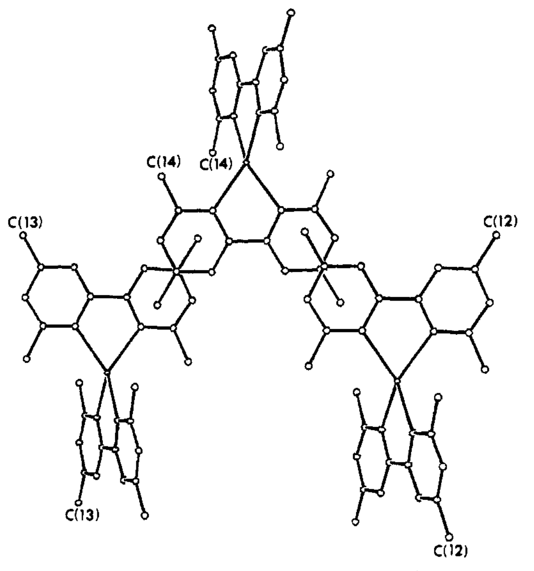

Figure 3. View of the stacking interactions in [Ag(tmbp)$_2$]BF$_4$. The view is down a line normal to the centermost tmbp ligand. Atoms labeled with the same numbers are related by a 2-fold axis.

in [Cu(dmbp)$_2$]BF$_4$,[14] and in [Cu(tmbp)$_2$]Cl·2H$_2$O.[17] Analogous interactions also help to stabilize edge-to-face contacts, which occur between stacks in crystalline systems[39] and between aromatic side chains in proteins.[40] The Coulombic contributions to the lattice energy can be significant; Williams estimates that they are responsible for 29% (about 15 kJ mol^{-1}) of the total lattice energy of crystalline benzene.[41]

In [Ag(tmbp)$_2$]BF$_4$ the Ag$^+$ and BF$_4^-$ ions are packed in layers separated by layers of (coordinated) tmbp ligands. Within the tmbp layers the packing of ligands is similar to that found in crystals of aromatic molecules such as 2,2′-bipyridine.[35] Thus, slipped stacks of approximately parallel ligand molecules (interplanar angle, 3.2 (4)°) run parallel to the *b* axis of the unit cell. Figure 3 illustrates some of the stacking interactions. The view is down a line normal to the central bipyridine ligand. The C(3) ring atom of one ligand is close to the C(8) ring atom on the next. This C(3)–C(8) distance is 3.64 (1) Å, and both C(3) and C(8) are 3.64 Å away from the mean plane of the adjacent pyridine rings. The C(12) methyl of one ligand is located approximately over the N(1) pyridine ring of the next with a C(12) to ring plane distance of 3.59 Å while the C(13) methyl group of the second ligand is located approximately over the center of the N(2) ring of the first, 3.71 Å from the plane of the ring. (Coulombic interactions may also occur between methyl hydrogens and adjacent rings, although the charge on hydrogen may be decreased when it is bonded to an sp^3 carbon compared with an sp^2 carbon.[42]) The individual stacks are arranged in a herringbone pattern with the mean planes of the ligands in one stack at an angle of 65.5 (1)° to those in adjacent stacks. The closest contacts between stacks are 3.42 (1) and 3.55 (1) Å between methyl groups. The isostructural [Cu(tmbp)$_2$]ClO$_4$ system packs similarly to the Ag(I) system, although there are small differences in distances and angles.[15]

It is evident that stacking interactions at the C(3) and C(8) positions exert a torque on the centermost ligand in Figure 3. Analogous interactions occur at its counterpart, opposite the Ag$^+$ ion, and together these interactions should favor a flattening distortion. Even though the stacking interactions comprise but a fraction of the total lattice energy, it seems clear that they mediate, if not control, the flattening.

It is worth noting in this regard that flattening distortions are likely to be relatively easily imposed in these systems. Favas and Kepert have emphasized the importance of repulsive forces between donor centers in determining the stereochemistry of metal complexes.[43] They have also suggested that pseudotetrahedral complexes, especially those with relatively large central ions, are likely to undergo flattening distortions quite easily when chelating ligands with small bite angles are involved. In these systems the strain energies associated with bringing pairs of donor atoms into proximity with each other is accounted for in the heat of formation of the ligand itself.

Finally, if intermolecular interactions are responsible for the flattening, we can expect that intramolecular steric interactions involving the 6- and 6′-methyl groups—C(11) and C(14) in Figure 1—will limit the distortion. And indeed, the methyl-to-methyl contacts are within 4 Å, or twice the van der Waals radius of the methyl group: distances are 3.81 and 3.79 Å between symmetry-related C(14) methyls in the Ag and Cu compounds, respectively, while the C(11) contacts are 3.91 and 3.84 Å for the same series.

Further Comparisons. We should note that several other workers have also concluded that stacking interactions are an important influence in systems involving aromatic ligands. Morpurgo and co-workers have identified significant stacking interactions in other Cu(I) systems,[44,45] while Purcell has suggested that such interactions are important in explaining cooperative magnetic effects in Fe(II) systems.[46] Sigel and co-workers have suggested that intramolecular stacking interactions can be important in determining stability constants,[47] and Sauvage and co-workers have found that intramolecular stacking interactions may induce irregular coordination geometries.[48] While this manuscript was under review, White and co-workers published crystal structures of the bis(1,10-phenanthroline)copper(I) ion in lattices with ClO$_4^-$ and CuBr$_2^-$ counterions.[49] Interligand dihedral angles of 49.9 and 76.8°, respectively, were observed, and it was suggested that cation–cation charge-transfer interactions were significant factors controlling crystal packing.[49] As a final point, it should be noted that if intermolecular stacking interactions produce these distortions in the solid state, the flattening distortion may be absent in the solution structures.

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Supplementary Material Available: Tables containing thermal parameters, hydrogen coordinates, C–C–C and F–B–F bond angles, and least-squares equations of planes (7 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (8 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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