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Novel Cu^{I} Ethylene Complexes with 6,6′-Diphenyl-4,4′-bipyrimidine Three-Dimensionally Self-Assembled by an Intermolecular π-π Stacking Interaction and a C–H···N Contact

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Four novel Cu^{I}–Ph$_2$bpm/C$_2$H$_4$ adducts [Cu(Ph$_2$bpm)(C$_2$H$_4$)]X [X = BF$_4$ (**1a**, **1b**), ClO$_4$ (**2**) and PF$_6$ (**3**); Ph$_2$bpm = 6,6′-diphenyl-4,4′-bipyrimidine] were prepared and they have been characterized by X-ray, ^{1}H NMR, IR and TG-DTA analyses. The molecular structures of Cu^{I}–Ph$_2$bpm/C$_2$H$_4$ complexes **1a**, **1b**, **2** and **3** are essentially similar: the Cu atom is coordinated by two N atoms in the chelate site of Ph$_2$bpm and the C=C bond of C$_2$H$_4$ in the trigonal-planar geometry. Interestingly, their crystal packing structures are much different from the connection manners of an intermolecular π–π stacking interaction and a C–H···N contact, resulting in the self-assembly of Cu^{I}–C$_2$H$_4$ adducts with a unique three-dimensional network structure. The X-ray, ^{1}H NMR, IR data support the assumption that the contribution of the larger Cu^{I}→C$_2$H$_4$ π back-donation bonding is induced by the electron-releasing phenyl group.

Introduction

Adducts of transition metals with alkenes have attracted a great amount of attention because of their potential applications in biochemistry, separation and catalysis, etc. Recently, structurally characterized coinage metal {Cu^{I}, Ag^{I}, Au^{I}}–C$_2$H$_4$ adducts were reviewed by Dias et al.[1] They have described that isolable and thermally stable coinage metal–C$_2$H$_4$ adducts are still limited and get increasingly sparse as one descends the group 11 triad towards gold. Coinage metal–C$_2$H$_4$ adducts with more than one C$_2$H$_4$ molecule at a metal center are rare. In particular, Cu^{I}–C$_2$H$_4$ adducts play an important role both in biochemistry and modern organic chemistry in relation to the copper receptor site ETR 1 of plant hormone[2] and Cu^{I}-based catalytic reaction.[3] Nevertheless, structurally Cu^{I}–C$_2$H$_4$ complexes are poorly characterized due to the extremely labile nature of the Cu^{I}–C$_2$H$_4$ interaction.[4–19] Most of Cu^{I}–C$_2$H$_4$ adducts are mononuclear complexes supported by bidentate or tridentate nitrogen ligands such as 2,2′-bipyridine and tris(pyrazolyl)borate.[1] Preparative and structural reports on polynuclear and polymeric Cu^{I}–C$_2$H$_4$ complexes are still scarce.[7,9,16,18]

By the way, 4,4′-bipyrimidine (bpm) and derivatives thereof are attractive nitrogen ligands with a bidentate site for chelation and two *exo*-N-donor sites for bridging since they can be thought of as a combination of 2,2′- and 4,4′-bipyridine. It is expected to produce both finite metallamacrocyclic and infinite polymeric compounds with square/rectangle motifs. However, only a few preliminary reports on coordination polymers of Cu^{I},[20,21] Ag^{I}[21,22] and Rh^{III},[23] together with mononuclear complexes of Ni^{II},[21] Ru^{II}[24–28] and Re^{I},[29] dinuclear complexes of Ru^{II}[30] and Ag^{I},[31] and trinuclear complex of Ru^{II}[32] can be found in the literature. In this study, we describe the preparation of new Cu^{I}–C$_2$H$_4$ adducts starting from complexes with 6,6′-diphenyl-4,4′-bipyrimidine (Ph$_2$bpm) as ligand. Four novel Cu^{I}–Ph$_2$bpm/C$_2$H$_4$ adducts that turned out to be three-dimensionally self-assembled by an intermolecular π–π stacking interaction and a C–H···N contact were isolated and characterized by X-ray, ^{1}H NMR, IR and TG-DTA analyses. There is growing interest in the relevance of weak supramolecular interactions, such as C–H···O and C–H···N hydrogen bonds[33–36] and π–π interactions,[37–40] for molecular packing and coordination in the context of supramolecular crystal engineering. It was found that these weak interactions can drive the crystallization process and select a particular molecular structure. However, little is still known about inorganic coordination complexes in contrast to organic and organometallic compounds. This study is expected to contribute to the field of design and architecture of Cu^{I} coordination polymers.

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Results and Discussion

Crystal Structures of Cu^I–Ph_2bpm/C_2H_4 Complexes

$[Cu(Ph_2bpm)(C_2H_4)]BF_4$ (1a, 1b)

The reaction of $[Cu(MeCN)_4]BF_4$ with Ph_2bpm in MeOH under C_2H_4 affords two kinds of products, small amounts of brick-shaped crystals (**1a**) and predominantly needle-like crystals (**1b**). The molecular structures of complexes **1a** and **1b** are shown in parts (a) and (b) of Figure 1. The Cu atom is coordinated by two N atoms in the chelate site of Ph_2bpm and the C=C bond of C_2H_4 in the trigonal-planar geometry in both complexes. Therefore, two terminal *exo*-bridging sites of Ph_2bpm are coordinatively unsaturated. In contrast to complex **1a**, it is interesting that the BF_4^- anion lies between two phenyl groups in complex **1b**. The dihedral angles between the planes defined by {C(1), C(2) and Cu(1)} and {N(2), N(4) and Cu(1)} atoms are 3.40 and 5.09° for complexes **1a** and **1b**, respectively. The average Cu–N and Cu–C distances are {1.989(2) and 2.004(2) Å} for **1a** and {1.9933(14) and 2.0064(14) Å} for **1b**. In the coordinated C_2H_4, the C=C distances of 1.382(3) (**1a**) and 1.374(2) Å (**1b**) are longer than that [1.313 (exp.) and 1.333 (calcd.) Å] of metal-free C_2H_4[41,42] and those [1.30(1)–1.366(6) Å] in the reported trigonal-planar Cu^I–C_2H_4 complexes,[5–11,18] indicative of the larger $Cu^I \rightarrow C_2H_4$ π back-donation bonding.[1] The selected bond lengths and bond angles of **1a** and **1b** are listed in Table 1.

Table 1. Selected bond lengths [Å] and bond angles [°] of Cu^I–Ph_2bpm/C_2H_4 complexes **1**–**3**.

(a) $[Cu(Ph_2bpm)(C_2H_4)]BF_4$ (**1a**)			
Cu(1)–N(2)	1.988(2)	Cu(1)–N(4)	1.990(2)
Cu(1)–C(1)	2.017(2)	Cu(1)–C(2)	1.990(2)
C(1)–C(2)	1.382(3)		
N(2)–Cu(1)–N(4)	82.52(8)	N(2)–Cu(1)–C(1)	123.21(9)
N(2)–Cu(1)–C(2)	163.53(8)	N(4)–Cu(1)–C(1)	154.02(9)
N(4)–Cu(1)–C(2)	113.83(9)	C(1)–Cu(1)–C(2)	40.35(10)
Cu(1)–N(2)–C(3)	129.35(17)	Cu(1)–N(2)–C(4)	114.14(15)
Cu(1)–N(4)–C(7)	128.73(17)	Cu(1)–N(4)–C(8)	114.18(15)
Cu(1)–C(1)–C(2)	68.76(14)	Cu(1)–C(2)–C(1)	70.89(14)
(b) $[Cu(Ph_2bpm)(C_2H_4)]BF_4$ (**1b**)			
Cu(1)–N(2)	1.9945(14)	Cu(1)–N(4)	1.9921(14)
Cu(1)–C(1)	1.9979(18)	Cu(1)–C(2)	2.0148(18)
C(1)–C(2)	1.374(2)		
N(2)–Cu(1)–N(4)	82.69(5)	N(2)–Cu(1)–C(1)	116.65(6)
N(2)–Cu(1)–C(2)	156.36(7)	N(4)–Cu(1)–C(1)	160.66(7)
N(4)–Cu(1)–C(2)	120.65(7)	C(1)–Cu(1)–C(2)	40.05(7)
Cu(1)–N(2)–C(3)	129.39(12)	Cu(1)–N(2)–C(4)	113.63(11)
Cu(1)–N(4)–C(7)	130.00(11)	Cu(1)–N(4)–C(8)	113.46(11)
Cu(1)–C(1)–C(2)	70.64(11)	Cu(1)–C(2)–C(1)	69.31(10)
(c) $[Cu(Ph_2bpm)(C_2H_4)]ClO_4$ (**2**)			
Cu(1)–N(2)	1.996(5)	Cu(1)–N(4)	1.983(5)
Cu(1)–C(1)	1.993(6)	Cu(1)–C(2)	1.998(6)
C(1)–C(2)	1.370(9)		
N(2)–Cu(1)–N(4)	82.4(2)	N(2)–Cu(1)–C(1)	116.5(2)
N(2)–Cu(1)–C(2)	156.4(2)	N(4)–Cu(1)–C(1)	161.1(2)
N(4)–Cu(1)–C(2)	121.0(2)	C(1)–Cu(1)–C(2)	40.1(2)
Cu(1)–N(2)–C(3)	129.1(4)	Cu(1)–N(2)–C(4)	113.6(4)
Cu(1)–N(4)–C(7)	129.5(4)	Cu(1)–N(4)–C(8)	114.5(3)
Cu(1)–C(1)–C(2)	70.2(3)	Cu(1)–C(2)–C(1)	69.7(3)
(d) $[Cu(Ph_2bpm)(C_2H_4)]PF_6$ (**3**)			
Cu(1)–N(2)	1.982(3)	Cu(1)–N(4)	1.989(4)
Cu(1)–C(1)	2.006(4)	Cu(1)–C(2)	2.000(4)
C(1)–C(2)	1.371(7)		
N(2)–Cu(1)–N(4)	82.86(16)	N(2)–Cu(1)–C(1)	119.18(18)
N(2)–Cu(1)–C(2)	159.15(19)	N(4)–Cu(1)–C(1)	157.73(18)
N(4)–Cu(1)–C(2)	117.99(19)	C(1)–Cu(1)–C(2)	40.0(2)
Cu(1)–N(2)–C(3)	129.6(3)	Cu(1)–N(2)–C(4)	113.4(3)
Cu(1)–N(4)–C(7)	129.8(3)	Cu(1)–N(4)–C(8)	113.6(3)
Cu(1)–C(1)–C(2)	69.7(2)	Cu(1)–C(2)–C(1)	70.3(2)

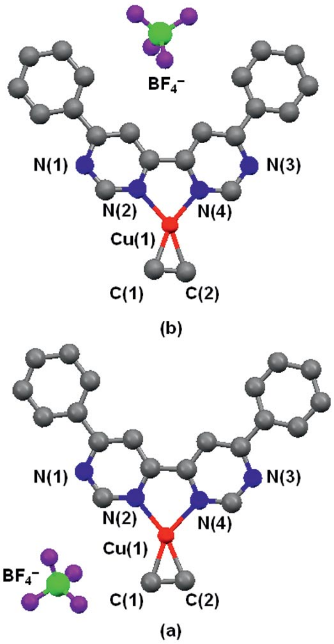

Figure 1. The molecular structures of $[Cu(Ph_2bpm)(C_2H_4)]BF_4$. (a) brick-shaped crystals **1a** and (b) needle-like crystals of **1b**.

The crystal packing structures of **1a** and **1b** are shown in Figures 2 and 3, respectively. Despite their similar molecular structures, it is to be noted that their crystal packing structures are much different from the connection manners of an intermolecular π–π stacking interaction and a C–H···N contact. In complex **1a**, each $[Cu(Ph_2bpm)(C_2H_4)]^+$ cation moiety is contacted along the *b*-axis to form a coplanar 1D-chain structure through the C–H···N contact [N(3)···C(14′) 3.522 Å] at the N(3) atom in the terminal *exo*-bridging site and the H atom with the C(14′) atom in the neighboring phenyl group. Additionally, there are two kinds of (i) the intermolecular π–π stacking interaction between two symmetric pyrimidine rings with the N(3) and N(3′′) atoms [centroid···centroid distance and interplanar angle between two rings are 3.597 Å and 0°; nearest C(8)···C(10′′) 3.317 Å], and (ii) the intermolecular π–π stacking interaction between two symmetric phenyl rings with the C(12) and C(13′′′) atoms [centroid···centroid distance and interplanar angle between two rings are 3.763 Å and 0°; nearest C(12)···C(13′′′) 3.376 Å]. In consequent, the four 1D Cu^I–Ph_2bpm/C_2H_4 chains are in parallel multi-layered along the *c*-axis, through the intermolecular π–π stacking interactions between the pyrimidine ring with the N(3) atom and phenyl ring with C(11′′′′) atom [centroid···centroid distance and interplanar angle between two rings are 3.651 Å and 1.53°; nearest C(10)···C(11′′′′) 3.384 Å and C(8)···C(13′′′′) 3.339 Å]. The intermolecular π–π–π–π stacking interactions in the basic unit of {pyrimidine ring}–{pyrimidine ring}–{phenyl ring}–{phenyl ring} are repeated along the *c*-axis.

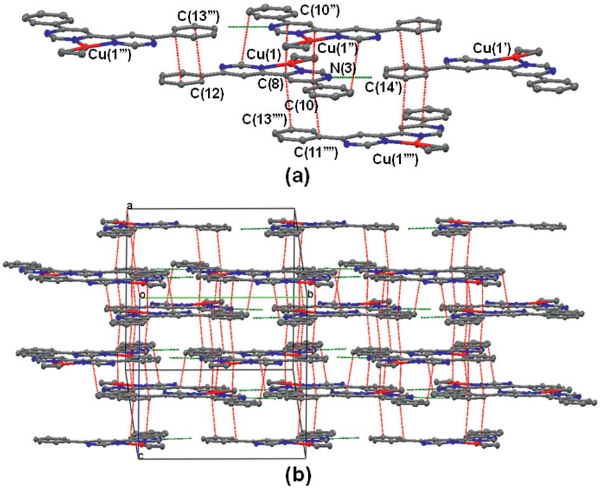

Figure 2. The crystal packing structures of [Cu(Ph$_2$bpm)(C$_2$H$_4$)]BF$_4$ (**1a**). (a) partial and (b) extended structures. The BF$_4^-$ anions were omitted for clearly.

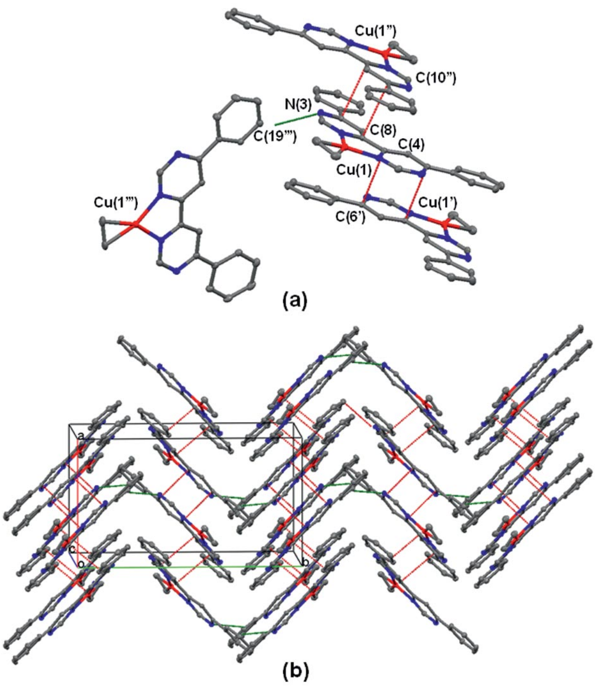

Figure 3. The crystal packing structures of [Cu(Ph$_2$bpm)(C$_2$H$_4$)]BF$_4$ (**1b**). (a) partial and (b) extended structures. The BF$_4^-$ anions were omitted for clearly.

On the other hand, the [Cu(Ph$_2$bpm)(C$_2$H$_4$)]$^+$ cation moieties in complex **1b** are properly oriented to each other to adopt the face-to-face configuration. There are two kinds of (i) intermolecular π–π stacking interactions between two symmetric pyrimidine rings with the N(1) and N(1′) atoms [centroid···centroid distance and interplanar angle between two rings are 3.623 Å and 0°; nearest C(4)···C(6′) 3.239 Å], and (ii) intermolecular π–π stacking interactions between two symmetric pyrimidine rings with the N(3) and N(3″) atoms [centroid···centroid distance and interplanar angle between two rings are 3.557 Å and 0°; nearest C(8)···C(10″) 3.271 Å]. The intermolecular π–π–π stacking interactions in the basic unit of {pyrimidine ring}–{pyrimidine ring}–{pyrimidine ring} are formed along the *a*-axis (Figure 3). Consequently, two columns of multi-stacking Cu^I–Ph$_2$bpm/C$_2$H$_4$ molecules are correlated through the C–H···N contact [N(3)···C(19′′′) = 3.268 Å] at the N(3) atom in the terminal *exo*-bridging site and the H atom with the C(19′′′) atom in the neighboring phenyl group. The zigzag chain structures of [Cu(Ph$_2$bpm)(C$_2$H$_4$)]$^+$ cation moiety are constructed along the *b*-axis.

[Cu(Ph$_2$bpm)(C$_2$H$_4$)]ClO$_4$ (2)

The molecular structure of complex **2** resembles to that of complex **1b**. The Cu atom is coordinated by two N atoms in the chelate site of Ph$_2$bpm and the C=C bond of the C$_2$H$_4$ molecule in the trigonal-planar geometry, with the dihedral angle of 3.89° between the planes defined by {C(1), C(2) and Cu(1)} and {N(2), N(4) and Cu(1)}. The ClO$_4^-$ anion is located between two phenyl groups. The average Cu–N and Cu–C distances are 1.989(5) and 1.995(6) Å, respectively. The coordinated C=C distance of 1.370(9) Å is longer than that [1.313 (exptl.) and 1.333 (calcd.) Å] of metal-free C$_2$H$_4$[41,42] and the C=C distance is close to those [1.382(3), 1.374(2) Å] of complexes **1a** and **1b**. The selected bond lengths and bond angles of complex **2** are listed in Table 1.

The crystal packing structure of complex **2** is also similar to that of complex **1b**. There are (i) intermolecular π–π stacking interactions between two symmetric pyrimidine rings with the N(1) and N(1′) atoms [centroid···centroid distance and interplanar angle between two rings are 3.638 Å and 0°; nearest C(4)···C(6′) 3.305 Å], and (ii) intermolecular π–π stacking interactions between two symmetric pyrimidine rings with the N(3) and N(3″) atoms [centroid···centroid distance and interplanar angle between two rings are 3.525 Å and 0°; nearest C(8)···C(10″) 3.271 Å]. Furthermore, each of Cu^I–Ph$_2$bpm/C$_2$H$_4$ molecule is correlated through the C–H···N contact [N(3)···C(19′′′) 3.280 Å]. As a result, the 3D network of [Cu(Ph$_2$bpm)(C$_2$H$_4$)]$^+$ cation moieties is formed by the intermolecular π–π–π stacking interactions along the *a*-axis and the C–H···N contacts along the *b*-axis.

[Cu(Ph$_2$bpm)(C$_2$H$_4$)]PF$_6$ (3)

The molecular structure of complex **3** is similar to those of complex **1b** and **2**. The PF$_6^-$ anion lies between two phenyl groups. The average Cu–N and Cu–C distances are

1.985(4) and 2.003(4) Å, respectively. As well as complexes **1a**, **1b** and **2**, the coordinated C=C distance of 1.371(7) Å is longer than that [1.313(exptl.) and 1.333(calcd.) Å] of metal-free C_2H_4[41,42] and those [1.30(1)–1.366(6) Å] in the reported trigonal-planar Cu^I–C_2H_4 complexes.[5–11,18] In a series of Cu^I–Ph_2bpm/C_2H_4 complexes, these findings suggest that the contribution of the larger π back-donation bonding is induced by the electron-releasing phenyl group in Ph_2bpm.[1,43] The selected bond lengths and bond angles of complex **3** are listed in Table 1.

The crystal packing structure of complex **3** is represented in Figure 4. It is remarkable that the crystal packing structure of complex **3** is different from those of **1a**, **1b** and **2**. Each $[Cu(Ph_2bpm)(C_2H_4)]^+$ cation moiety is located in the face-to-face configuration. The intermolecular short contact of C(10)···C(20′) 3.382 Å [centroid···centroid distance and interplanar angle between two rings are 3.771 Å and 11.49°] is between the C(10) atom of pyrimidine ring with the N(3) atom and the C(20′) atom of neighboring phenyl ring, resulting in the self-assembly of a unique 1D stair-shaped structure by the connections of $[Cu(Ph_2bpm)(C_2H_4)]^+$ cation moieties.

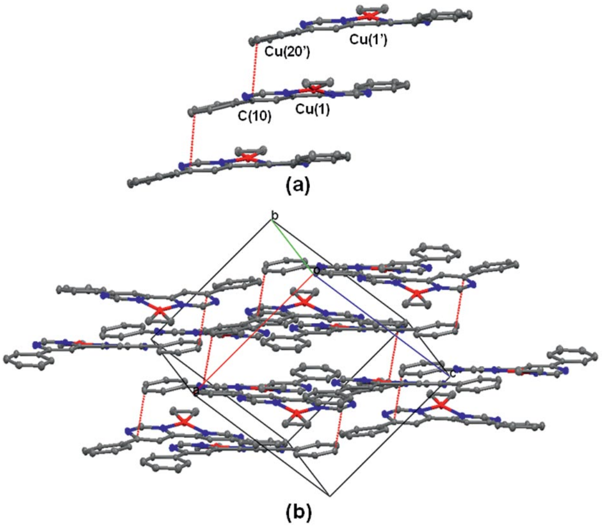

Figure 4. The crystal packing structures of $[Cu(Ph_2bpm)(C_2H_4)]PF_6$ (**3**). (a) partial and (b) extended structures. The PF_6^- anions were omitted for clearly.

^1H NMR, IR Spectra and TG-DTA Curves of Cu^I–Ph_2bpm/C_2H_4 Complexes

We have attempted to determine the structures of **1**–**3** in solution by ^1H NMR method. However, these Cu^I–C_2H_4 adducts are only poorly soluble in commonly used organic solvents. Complexes **1** and **3** are slightly soluble in CD_2Cl_2. Adduct **3**, dissolved in CD_2Cl_2 gave four well-resolved ^1H NMR resonances at 23 °C without any signals of dissociation species. The ^1H NMR resonances in the coordinated Ph_2bpm ligand are shifted downfield relative to metal-free Ph_2bpm ligand [δ = 9.32(2–H), 8.87(5–H), 8.20(C_6H_5) and 7.50(C_6H_5)], with the coordination shifts ($\Delta\delta = \delta_{complex} - \delta_{metal\text{-}free}$) of 0.01–0.12, except for the 5-H signal ($\Delta\delta$ = –0.13 ppm). In contrast, one sharp ^1H NMR resonance is observed for coordinated C_2H_4 at δ = 4.98, which is shifted upfield relative to metal-free C_2H_4 (δ = 5.24 ppm), indicative of $Cu^I{\rightarrow}C_2H_4$ π back-donation bonding.[1] The chemical shift value is within the range of those reported for trigonal-planar Cu^I–C_2H_4 complexes (δ = 4.48–5.28).[5,9,18,43] In comparison with complex **3**, adduct **1**, dissolved in CD_2Cl_2 shows slightly broad ^1H NMR signals at 23 °C. The ^1H NMR resonances in the coordinated Ph_2bpm ligand are also shifted downfield relative to the metal-free Ph_2bpm ligand, with $\Delta\delta$ values of 0.07–0.12, except for the 5-H signal ($\Delta\delta$ = –0.02 ppm). The coordinated C_2H_4 give rise to one slightly broadened ^1H NMR resonance at δ = 5.08, which is shifted upfield relative to metal-free C_2H_4. These results prove that the structures of Cu^I–Ph_2bpm/C_2H_4 adducts **1** and **3** are maintained in solution.

The $\nu_{C=C}$ bands of the coordinated ethylene in **1**–**3** are observed at 1531, 1529 and 1530 cm^{-1}, respectively. These $\nu_{C=C}$ bands show a lower frequency shift relative to metal-free C_2H_4 ($\nu_{C=C}$ = 1623 cm^{-1}), and these values are within the range of those reported for trigonal-planar Cu^I–C_2H_4 complexes (1515–1537 cm^{-1}),[5,8,10,18,43] indicative of $Cu^I{\rightarrow}C_2H_4$ π back-donation bonding. The IR and ^1H NMR spectroscopic data are consistent with crystallographic data.

Thermogravimetric analysis (TG-DTA) was carried out under flowing N_2 gas for **1** and **3** (Figure 5). Complex **1** sustained a total mass loss of 5.9% (calcd. 5.7%) with the relatively gentle curve at 210–275 °C, this corresponds to loss of one C_2H_4 molecule. Similarly, complex **3** lost 5.9% (calcd. 5.1%) of its mass (relatively gentle curve at 80–265 °C), corresponding to loss of one C_2H_4 molecule. It is suggested that Cu^I–Ph_2bpm/C_2H_4 adducts of type **1** and **3** are thermally stable.

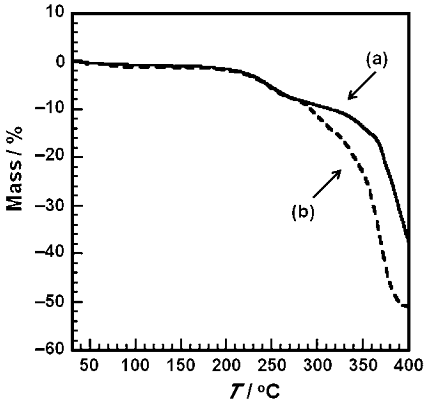

Figure 5. TG-DTA curves of complexes **1** and **3** under flowing N_2 gas. (a) solid line for complex **1** and (b) broken line for complex **3**.

Conclusions

It is known that planar coordination compounds with aromatic ligands, especially having extended π-systems, show π–π stacking interaction in the solid states. In alkene or alkyne π-bonded Cu^I complexes, in-plane coordination of a C=C or C≡C bond to trigonal planar Cu^I centers often leads to planar molecular conformations.[5,6,9,44,45] For instance, the infinite π–π stacking columns are confirmed in 2,2′-bipyridine complex $[Cu(2,2'\text{-bpy})(CH_2{=}CH_2)]ClO_4$[6] and 1,10-phenanthroline complex $[Cu(1,10\text{-phen})(CH{\equiv}CCO_2Et)]ClO_4$[45] with the nearest carbon-to-carbon distances of 3.31 and 3.37 Å, respectively, while dimer formation through π–π stacking interaction can be seen in a Cu^I–alkyne complex $[Cu(1,10\text{-phen})(CH{\equiv}CH)]ClO_4$[45] (the nearest carbon-to-carbon distances being 3.42 Å).

In contrast, the bpm ligand is a multidentate nitrogen ligand with a bidentate site for chelation and two *exo*-N-donor sites for bridging, as mentioned in the introduction. In this study, we found that the Ph_2bpm ligand with a phenyl group can produce novel Cu^I–C_2H_4 adducts that are three-dimensionally self-assembled by intermolecular π–π stacking interactions and C–H···N contacts. It is proved that the contribution of the larger π back-donation bonding is induced by the electron-releasing phenyl group. These new findings are expected to contribute toward design and architecture of structurally new Cu^I–C_2H_4 adducts.

Experimental Section

General Procedures and Reagents: The precursor Cu^I complexes $[Cu(MeCN)_4]X$ (X = PF_6 and BF_4) were prepared according to the literature.[46] $Cu(ClO_4)_2{\cdot}6H_2O$ and Cu wire were purchased from Mitsuwa Chemicals (Japan) and used without further purification. 6,6′-Diphenyl-4,4′-bipyrimidine (Ph_2bpm) was prepared by a modified literature method.[47] The pure C_2H_4 gas (>99.9%) was purchased from Sumitomo Seika (Japan). All organic solvents were dried and distilled by usual methods before use. All procedures were carried out using standard Schlenk techniques under C_2H_4. IR spectra were recorded with a JASCO FT-IR 430 spectrometer as KBr pellets. ^1H NMR spectra were measured by JEOL JNM AL-400 and JNM ECA-500 NMR spectrometers. Thermogravimetric analysis (TG-DTA) was recorded by RIGAKU Thermo Plus 8120 under flowing N_2 gas.

Preparation of Cu^I–Ph_2bpm/C_2H_4 Complexes

$[Cu(Ph_2bpm)(C_2H_4)]BF_4$ (1a, 1b): $[Cu(MeCN)_4]BF_4$ (31.6 mg, 10.0 mmol) and Ph_2bpm (3.2 mg, 1.0 mmol) were reacted in MeOH (10 mL) under C_2H_4. The reaction solution was filtered and the filtrates were sealed in glass tubes (7 mm inner diameter) under C_2H_4. The reaction solution was allowed to stand for one week at –5 °C. A small amount of yellow brick-shaped crystals (**1a**) was collected, together with a bulk of yellow needle-like crystals (**1b**). After drying in a flow of C_2H_4 gas the crystals were immediately subjected to characterization. Yield 4.0 mg (82%). $C_{22}H_{18}BCuF_4N_4$ (488.76): calcd. C 54.06, H 3.71, N 11.46; found C 53.72, H 4.53, N 11.56. ^1H NMR (500Mz, CD_2Cl_2, 23 °C): δ = 9.39 (s, 1 H, 2-H), 8.89 (s, 1 H, 5-H), 8.45–8.37 (m, 2 H, C_6H_5) and 7.71–7.65 (m, 3 H, C_6H_5) for Ph_2bpm; 5.08 (s, 1 H) for C_2H_4 ppm. IR (KBr): $\tilde{\nu}$ = 1593 (s), 1531 (s, C_2H_4), 1515 (s), 1466 (s), 1440 (m), 1431 (m), 1391 (s), 1282 (s), 1262 (m), 1244 (m), 1187 (m), 1123–960 (s, BF_4), 798 (m), 749 (s), 690 (s), 676 (m), 647 (m), 637 (s), 540 (m), 517 (m), 409 (m) cm^{-1}.

$[Cu(Ph_2bpm)(C_2H_4)]ClO_4$ (2): The precursor Cu^I–C_2H_4 complex $[Cu(C_2H_4)_n]ClO_4$ was prepared by reductive reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ (74.1 mg, 2.0 mmol) with Cu wire in MeOH (5 mL) under C_2H_4. A solution of Ph_2bpm (4.8 mg, 1.5 mmol) in 5 mL of MeOH was added to the above Cu^I–C_2H_4 solution. C_2H_4 gas was bubbled through the solution for a further 30 min. Then the pale yellow solution was filtered and the filtrates were sealed in glass tubes (7 mm inner diameter) under C_2H_4. The reaction solution was allowed to stand at –5 °C for two weeks; after this time, brown brick-shaped crystals of complex **2** could be collected. Complex **2** was dried in a flow of C_2H_4 gas and then immediately used to measure IR spectroscopic data. Microanalysis and TG-DTA was not performed since **2** tends to explode when heated (see safety remark below). Yield 4.0 mg (80%). IR (KBr): $\tilde{\nu}$ = 1592 (s), 1529 (s, C_2H_4), 1513 (s), 1465 (s), 1440 (m), 1430 (m), 1390 (s), 1281 (s), 1262 (m), 1243 (m), 1186 (m), 1105–1060 (s, ClO_4), 1012 (s), 794 (m), 959 (m), 927 (m), 899 (m), 798 (m), 749 (s), 690 (s), 676 (m), 647 (m), 637 (s), 621 (s), 541 (m), 409 (m) cm^{-1}.

Caution! Perchlorate salts of metal complexes with organic compounds are potentially explosive! Only small amounts of materials should be prepared and handled with great care.

$[Cu(Ph_2bpm)(C_2H_4)]PF_6$ (3): $[Cu(MeCN)_4]PF_6$ (7.6 mg, 2.0 mmol) and Ph_2bpm (3.2 mg, 1.0 mmol) were reacted in MeOH (10 mL) under C_2H_4. The reaction solution was filtered and the filtrates were sealed in glass tubes (7 mm inner diameter) under C_2H_4. The reaction solution was allowed to stand for one week at –5 °C. Colorless plate-like crystals of **3** were obtained. After drying in a flow of C_2H_4 gas, **3** was immediately used to measure elementary analysis, IR, ^1H NMR spectra and TG-DTA. Yield 4.8 mg (88%). $C_{22}H_{18}CuF_6N_4P$ (546.92): calcd. C 48.31, H 3.32, N 10.24; found C 48.41, H 3.93, N 8.88. ^1H NMR (400 MHz, CD_2Cl_2, 23 °C): δ = 9.33 (s, 1 H, 2-H), 8.74 (s, 1 H, 5-H), 8.32 (m, 2 H, C_6H_5) and 7.60 (m, 3 H, C_6H_5) for Ph_2bpm; 4.98 (s, 1 H) for C_2H_4 ppm. IR (KBr): $\tilde{\nu}$ = 1603 (s), 1530 (s, C_2H_4), 1518 (s), 1465 (s), 1444 (m), 1427 (m), 1393 (s), 1279 (s), 1265 (s), 1240 (m), 1185 (m), 1173 (m), 1104 (m), 1075 (m), 1017 (s), 1007 (m), 889–748 (s, PF_6), 749 (s), 689 (s), 677 (m), 648 (m), 638 (m), 557 (s), 409 (m) cm^{-1}.

X-ray Crystal Structure Determinations: All measurements of Cu^I–Ph_2bpm/C_2H_4 complexes **1a**, **1b**, **2** and **3** were made on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71070 Å). The diffraction data were collected at –165 °C for complexes **1a** and **1b**, and –155 °C for complexes **2** and **3** by the ω scan mode. Of the 22885, 23101, 23479 and 24603, reflections which were collected, 4605, 4633, 4891 and 4669 were unique (R_{int} = 0.053, 0.036, 0.127 and 0.036) for complexes **1a**, **1b**, **2** and **3**, respectively. Data were collected and processed using Crystal Clear program (Rigaku). The linear absorption coefficient, μ, for Mo-K_α radiation is 11.377, 11.305, 12.380 and 11.655 cm^{-1} for complexes **1a**, **1b**, **2** and **3**, respectively. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (*SIR*-97 for complexes **1a**, **1b**, **2** and **3**) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4605, 4633, 4669 and 4891 observed reflections (all data) for complexes **1a**, **1b**, **2** and **3**, respectively. The unweighted and weighted agreement factors of R were used (see footnote of Table 2). The R, $R1$ and $wR2$ values were {0.0599, 0.0482 and 0.0943}, {0.0396, 0.0343 and 0.0800}, {0.1430, 0.0994 and 0.2010} and {0.1101, 0.0982 and 0.1436} for complexes **1a**, **1b**, **2** and **3**, respectively. All calculations were performed using the Crystal Structure 3.8.2 Crystal Structure Analysis Package (Rigaku and Rigaku Americas).

Table 2. Crystallographic data of Cu^I–Ph_2bpm/C_2H_4 complexes **1**–**3**.[a]

	$[Cu(Ph_2bpm)(C_2H_4)]BF_4$ (**1a**)	$[Cu(Ph_2bpm)(C_2H_4)]BF_4$ (**1b**)	$[Cu(Ph_2bpm)(C_2H_4)]ClO_4$ (**2**)	$[Cu(Ph_2bpm)(C_2H_4)]PF_6$ (**3**)
Formula	$C_{22}H_{18}CuN_4BF_4$	$C_{22}H_{18}CuN_4BF_4$	$C_{22}H_{18}CuN_4ClO_4$	$C_{22}H_{18}CuN_4PF_6$
Formula weight	488.76	488.76	501.41	546.92
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/a$
a [Å]	12.597(7)	9.470(4)	9.5216(17)	10.391(6)
b [Å]	13.699(6)	16.483(7)	16.362(2)	19.422(10)
c [Å]	13.223(7)	13.012(6)	13.152(2)	10.710(6)
β [°]	117.908(6)	92.267(5)	93.459(11)	97.659(7)
V [Å^3]	2016.5(17)	2029.4(16)	2045.2(6)	2142.1(20)
Z	4	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.610	1.610	1.628	1.696
$F(000)$	992.0	992.0	1024.0	1104.0
μ (Mo-K_α) [cm^{-1}]	11.377	11.305	12.380	11.655
Temperature [K]	108	108	118	118
Total number of refl.	22885	23101	23479	24603
Measured refl.	4605 (unique, R_{int} = 0.053)	4633 (unique, R_{int} = 0.036)	4669 (unique, R_{int} = 0.127)	4891(unique, R_{int} = 0.036)
Observed refl.	4605 (all reflections)	4633 (all reflections)	4669 (all reflections)	4891 (all reflections)
R	0.0599 (all reflections)	0.0396 (all reflections)	0.1430 (all reflections)	0.1101 (all reflections)
$R1$	0.0482 [$I > 2\sigma(I)$]	0.0343 [$I > 2\sigma(I)$]	0.0994 [$I > 2\sigma(I)$]	0.0982 [$I > 2\sigma(I)$]
$wR2$	0.0943	0.0800	0.2010	0.1436

[a] $R = \Sigma||F_o| - |F_c|/\Sigma|F_o|$. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Crystal data and details of the structure determination are summarized in Table 2. CCDC-735990 (for **1a**), -735991 (for **1b**), -735992 (for **2**), -735993 (for **3**) contains the supplementary crystallographic data for complexes **1a**, **1b**, **2** and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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