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Structures and Spectral Properties of Some Bis(carboxylato)copper(II)-Pyrazole Complexes. I. Preparation of Bis(trifluoroacetato)tetrakis(pyrazole)copper(II)

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The preparation of several kinds of [Cu(tfa)$_2$(Hpzl)$_4$] (Htfa=trifluoroacetic acid; Hpzl=1*H*-pyrazoles) by stoichiometric reactions of [Cu(hfac)$_2$] (Hhfac=1,1,1,5,5,5-hexafluoro-2,4-pentanedione) with a pyrazole in petroleum ether is reported. As isolable intermediate of this reaction, [Cu(hfac)$_2$(Hpzl)$_4$] was obtained in some cases. The structure of [Cu(tfa)$_2$(4-Hmpz)$_4$] (**1e**) (4-Hmpz=4-methyl-1*H*-pyrazole) has been determined by X-ray analysis. The structures of other [Cu(tfa)$_2$(Hpzl)$_4$] are estimated on the basis of their IR spectra.

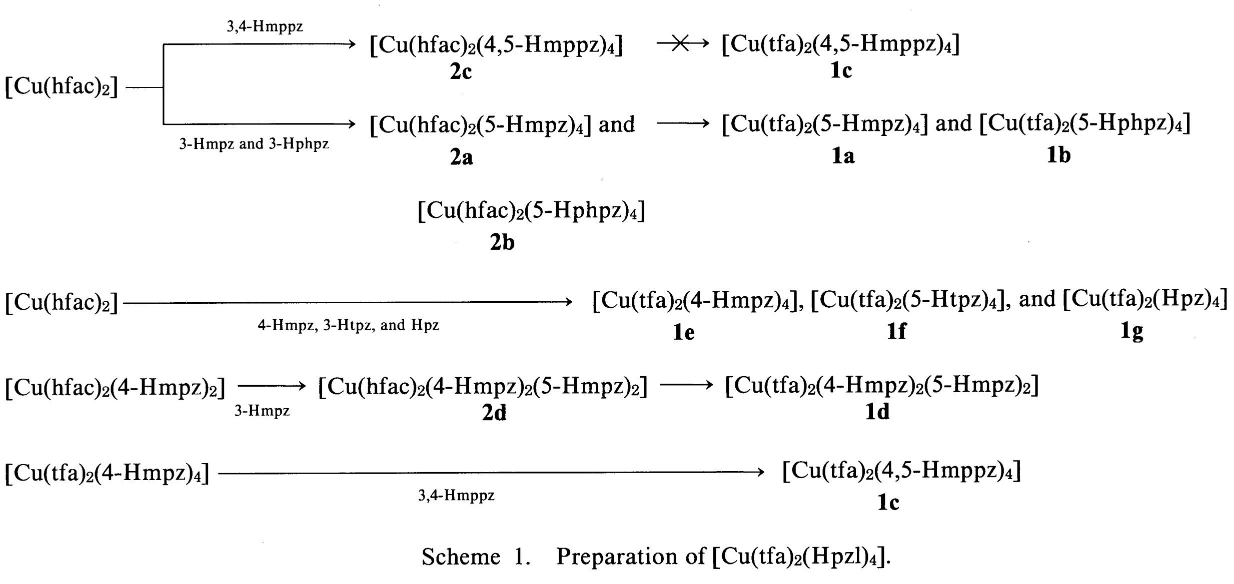
Recently, many metal complexes of 1*H*-pyrazoles have been investigated,[1] and some of them are reaction products of bis(β-diketonato)copper(II) complexes with 1*H*-pyrazoles.[2–4] The complexation reactions of bis(β-diketonato)copper(II) with 1*H*-pyrazoles are very sensitive to the nature of the 1*H*-pyrazole and β-diketonato ligand as well as to the reaction conditions, sometimes giving different products depending upon the solvent used. For example, the reaction of [Cu(hfac)$_2$] (Hhfac=1,1,1,5,5,5-hexafluoro-2,4-pentanedione) with 3-methyl-1*H*-pyrazole (3-Hmpz) gave 1 : 1 and 1 : 4 adducts.[3] On the other hand, 4-methyl-1*H*-pyrazole (4-Hmpz) gave 1 : 1, 1 : 2, and 1 : 3 adducts, and 1 : 4 adduct was not isolable from a solution of the 1 : 4 reactant mixture.[4] In this reaction, we found that [Cu(tfa)$_2$(4-Hmpz)$_4$] (Htfa=trifluoroacetic acid) can be obtained, though the reaction of [Cu(tfa)$_2$] with 4-methyl-1*H*-pyrazole do not give this complex.

A related compound, [Cu(tfa)$_2$(py)$_4$] has been prepared by the reaction of [Cu(hfac)$_2$] with pyridine,[5] and the reaction of [Cu(tfa)$_2$] with pyridine also gave the same complex,[6] on which X-ray analyses have been made.[5,7]

This paper reports the preparative methods and the structures of several [Cu(tfa)$_2$(Hpzl)$_4$] complexes.

Results and Discussion

Recently we observed that the reactions of [Cu(tfa)$_2$] with 1*H*-pyrazole gave μ-pyrazolato complexes instead of the expected complexes of [Cu(tfa)$_2$(Hpzl)$_4$] (**1**). For example, the reaction of [Cu(tfa)$_2$] with 1*H*-pyrazole (Hpz) gave a purple or a brown precipitate [Cu(μ-pz)$_2\cdot n$H$_2$O][8] (n=1/2 and 1), and 3-Hmpz molecule gave a green precipitate [Cu(μ-3-mpz)$_2$].[9] We also found that several [Cu(tfa)$_2$(Hpzl)$_4$] complexes can be obtained by the reaction of [Cu(hfac)$_2$] with 1*H*-pyrazoles. As isolable intermediate of this reaction, [Cu(hfac)$_2$(Hpzl)$_4$]



Scheme 1. Preparation of [Cu(tfa)$_2$(Hpzl)$_4$].

Table 1. Diffuse Reflectance and IR Spectral Data of the tfa Complexes

Complex	λ_{max}/nm		ν(N–H)/cm^{-1}	ν(C=O)/cm^{-1}	ν(C–O)/cm^{-1}
1a [Cu(tfa)$_2$(5-Hmpz)$_4$]	584		3337	1677	1432
1b [Cu(tfa)$_2$(5-Hphpz)$_4$]	585	732	3255	1670	1422
1c [Cu(tfa)$_2$(4,5-Hmppz)$_4$]	578		3285	1671	1432
1d [Cu(tfa)$_2$(4-Hmpz)$_2$(5-Hmpz)$_2$]	593		3348	1675	1432
1e [Cu(tfa)$_2$(4-Hmpz)$_4$]	576		3350	1671	1434
1f [Cu(tfa)$_2$(5-Htpz)$_4$]	598	ca.730	3280	1669	1432
1g [Cu(tfa)$_2$(Hpz)$_4$]	588		3309	1671	1438

(**2**) was obtained in some cases, although an alternate path which produces the complex **1** directly can not be excluded. The newly prepared complexes, [Cu(tfa)$_2$(Hpzl)$_4$] are listed in Table 1 with spectral data.

As shown in Scheme 1, **1a** and **1b** were obtained by decomposition of **2a** and **2b** in petroleum ether, respectively, while [Cu(hfac)$_2$] reacts with 4-Hmpz molecules to give **1e** directly.

On the other hand, **1c** and **1d** were prepared by alternate methods. **1d** was obtained by decomposition of **2d**, which was isolated by the reaction of [Cu(hfac)$_2$(4-Hmpz)$_2$] with 3-Hmpz molecules.

These reactions are very sensitive to the reaction conditions. For example, while **2a** was crystallized from cyclohexane, it was decomposed to yield **1a** in petroleum ether. On the other hand, **2c** was not decomposed to yield **1c** in petroleum ether. Ligand exchange reaction of 3,4-Hmppz molecules with 4-Hmpz molecules in **1e** gave **1c**.

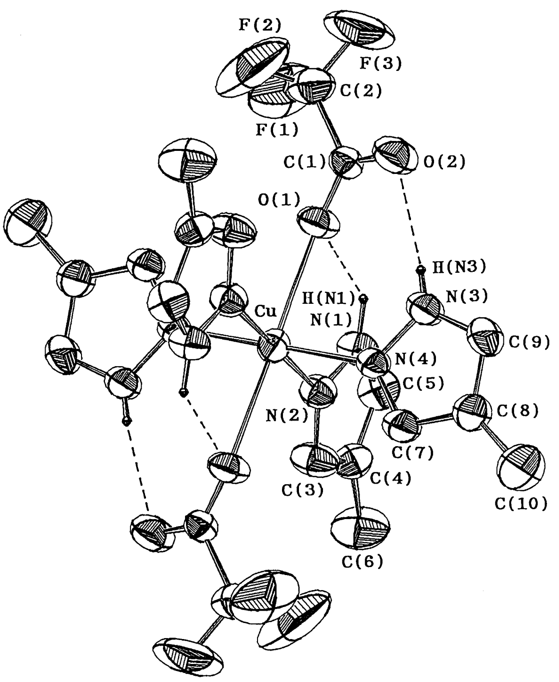


Fig. 1. A perspective drawing of the structure of **1e**, showing the numbering scheme of the atoms (50% probability thermal ellipsoids). Unlabeled atoms are related to labeled atoms by the inversion center. Only the H(N1) and H(N3) hydrogen atoms are shown, and the intramolecular hydrogen bonds are drawn.

It has been reported that in pyrazole complexes the coordinating nitrogen atom in pyrazole is the one which has less interaction than the other with the substituent group or groups in the molecule. For example, 3-methyl-1*H*-pyrazoles are coordinated in the form of 5-methyl-1*H*-pyrazole in **2a**.[3] Also in **2b** and **2c**, 5-Hphpz and 4,5-Hmppz (4-phenyl-5-methyl-1*H*-pyrazole) may be found. In **1a**, **1b**, and **1d**, the 5-substituted forms may be more favorable than the other tautomers, and in **1c** and **1f**, 4,5-Hmppz and 5-Htpz molecules may be found.

The mechanism of formation reaction of [Cu(tfa)$_2$(py)$_4$] has been discussed.[5] It is prepared from a pyridine solution of [Cu(hfac)$_2$] standing in contact with the atmosphere for several weeks. In this case, the hfac ligand is apparently hydrolyzed with C–C bond rupture under the conditions. In our experiment the tfa complexes may probably be formed by a similar mechanism.

Table 2. Final Atomic Coordinates ($\times 10^4$ Except for H and $\times 10^3$ for H), with Estimated Standard Deviations in Parentheses, and Their Equivalent Isotropic Temperature Factors, for **1e**

Atom	x	y	z	B_{eq}/Å^2
Cu	0	0	0	4.1
F(1)	−5625(3)	372(3)	−3388(4)	6.2
F(2)	−5301(3)	−1867(4)	−4626(4)	7.2
F(3)	−4905(4)	−1002(5)	−1886(5)	5.0
O(1)	−2355(3)	−430(2)	−2329(3)	4.6
O(2)	−2012(3)	−2848(3)	−3544(3)	4.5
N(1)	−1075(3)	1091(3)	−3028(3)	6.1
N(2)	−47(3)	1083(3)	−1438(3)	4.4
N(3)	1301(3)	−3118(3)	−2433(3)	5.2
N(4)	1648(3)	−1954(3)	−1197(3)	4.6
C(1)	−2822(4)	−1483(3)	−3055(4)	8.5
C(2)	−4663(4)	−1029(4)	−3266(5)	5.3
C(3)	707(4)	1941(4)	−1164(5)	5.2
C(4)	170(4)	2501(3)	−2563(4)	5.9
C(5)	−967(4)	1932(4)	−3723(4)	5.3
C(6)	720(5)	3537(5)	−2707(6)	8.8
C(7)	3274(4)	−2435(4)	−926(5)	5.2
C(8)	3969(4)	−3891(4)	−1983(5)	7.0
C(9)	2662(4)	−4282(3)	−2936(5)	6.4
C(10)	5761(5)	−4844(5)	−2024(7)	8.2
H(N1)	−171(4)	57(4)	−340(4)	6(1)[a]
H(N3)	44(3)	−303(3)	−283(4)	4(1)[a]

a) Isotropic temperature factor.

Table 3. Selected Bond Lengths and Bond Angles around the Copper Atom, with Estimated Standard Deviations in Parentheses, for **1e**

Bond length (l/Å)		Bond angle (ϕ/°)			
Cu–O(1)	2.452(3)	Cu–O(1)–C(1)	135.2(2)	O(1)–Cu–N(2)	85.4(1)
Cu–N(2)	2.012(3)	O(1)–Cu–N(4)	92.1(1)	N(2)–Cu–N(4)	90.5(1)
Cu–N(4)	2.013(3)	Cu–N(2)–N(1)	120.9(2)	Cu–N(2)–C(3)	134.4(3)
		Cu–N(4)–N(3)	125.4(2)	Cu–N(4)–C(7)	130.3(3)

It was observed that weaker bases i.e., Hpz molecule (pK_a=2.5) and 4-Hmpz molecule (pK_a=3.1) gave the tfa complexes **1e** and **1g** directly. In these weak bases, the intermediate **2** may probably be less stable. In spite of the weak basicity of 3-Hphpz molecule[10] (pK_a=2.1), it gave the intermediate **2b**. The stability of the intermediate **2b** and **2c** is probably due to the contribution of phenyl group to the resonance stabilization of the complex.[2,11,12] On the other hand, the presence of thienyl groups in the complex may have less stabilization effect on it, for the intermediate [Cu(hfac)$_2$(5-Htpz)$_4$] is not isolated.

Although pyridine (pK_a=5.2) is a rather stronger base, intermediate [Cu(hfac)$_2$(py)$_4$] has not been isolated. It has been shown that in unidentate hfac complexes,[3,13] coordinated hfac ligands are stabilized by the intramolecular hydrogen bonds. The intermediate [Cu(hfac)$_2$(py)$_4$] may be unstable because of no contribution of the intramolecular hydrogen bonds.

ORTEP projection of **1e** is shown in Fig. 1 with the atomic numbering. The final atomic coordinates of the complex is given in Table 2, and the geometry of the metal coordination sphere in Table 3.[14] The molecule has a center of symmetry and the geometry about each copper atom is approximately a tetragonal bipyramid, with the four nitrogen atoms from 4-Hmpz molecules in the equatorial plane and two oxygen atoms from each unidentate tfa ligand in the axial positions.

The basic structure of **1e** is similar to that of [Cu(tfa)$_2$(py)$_4$],[5,7] which also has a coordination of a tetragonal bipyramid, with four nitrogen atoms in the equatorial plane and two oxygen atoms from unidentate tfa ligands at the apexes.

The Cu–O(1) distance (2.452(3) Å) is somewhat longer than those of [Cu(tfa)$_2$(py)$_4$] (e.g., 2.361(4) and 2.350(4) Å[7]). The Cu–N(2) and Cu–N(4) distances (2.012(3) and 2.013(3) Å, respectively) are equal, and slightly shorter than those of [Cu(tfa)$_2$(py)$_4$]. For example, the Cu–N(1), Cu–N(2), Cu–N(3), and Cu–N(4) distances of it are 2.039(4), 2.052(3), 2.037(4), and 2.047(3) Å, respectively.[7]

In the IR spectra, ν(C=O) band of **1e** was observed at 1671 cm^{-1}, and this frequency is similar to those of other tfa complexes. Therefore, the basic structure of the tfa complexes may resemble that of **1e**.

The ν(N–H) bands were observed in the region of 3350—3255 cm^{-1} for these tfa complexes. For **1e**, the ν(N–H) bands assigned to the weak hydrogen bond, O(1)···H(N1)–N(1) and O(2)···H(N3)–N(3), were observed as a single band at 3350 cm.$^{-1}$ It may be an overlapped band. As Fig. 1 shows, these bonds are geometrically different, although the distances O(1)···N(1) and O(2)···N(3) are similar (2.823(5) and 2.826(4) Å, respectively) (Table 4). The Cu–N(2) and Cu–N(4) distances are equal (Table 3), and the bond lengths and the bond angles in the four 4-Hmpz molecules are also equal. The tfa ligands are planar and dihedral angles of 4-Hmpz molecules are 75.5° and 19.5°. In contrast to **2a**,[3] non-split ν(N–H) bands of the tfa complexes suggest that the four O···H–N hydrogen bonds are equal.

Table 4. Distances O···N (l/Å) and Angles O···H–N (ϕ/°) of Hydrogen Bonds for **1e**

O···N		O···H–N	
O(1)···N(1)	2.823(5)	O(1)···H(N1)–N(1)	138(3)
O(2)···N(3)	2.826(4)	O(2)···H(N3)–N(3)	170(4)
O(1)···N(3)	3.229(3)	O(1)···H(N3)–N(3)	128(3)

[Cu(tfa)$_2$(py)$_4$] loses pyridine when exposed to air, though it is stable under pyridine vapor. On the other hand, the tfa complexes **1** are stable on exposure to air. The larger stability of **1** than [Cu(tfa)$_2$(py)$_4$] may be due to the presence of the intramolecular hydrogen bonds in **1**.

The low ν(C=O) frequencies of **1** may probably arise from the intramolecular hydrogen bonds. In [Cu(tfa)$_2$(py)$_4$], the ν(C=O) and ν(C–O) frequencies are observed at 1690 and 1450 cm^{-1}, respectively.[6] The corresponding frequencies for **1e** are slightly lower.

The diffuse reflectance spectra of the tfa complexes **1** resemble that of **1e**, showing broad maxima in the region of 573—598 nm. It suggests that the coordination environments of these complexes are similar. This is in agreement with the IR data.

Experimental

Materials. Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) was prepared by the reported method.[15] 1*H*-Pyrazole (Hpz), 3-methyl-1*H*-pyrazole, 3-(2-thienyl)-1*H*-pyrazole (3-Htpz) (Tokyo Kasei Kogyo Co., Ltd.), 4-methyl-1*H*-pyrazole (Aldrich Chemical Co.), 3-methyl-4-phenyl-1*H*-pyrazole (3,4-Hmppz) (Lancaster Synthesis Ltd.) were used without further purification. 3-Phenyl-1*H*-pyrazole (3-Hphpz) was prepared by the reported method.[16] Found: C, 75.09; H, 5.38; N, 19.16%. Calcd for $C_9H_8N_2$: C, 74.98; H, 5.59; N, 19.43%.

Preparation of the Complexes. [Cu(hfac)$_2$(5-Hmpz)$_4$] (**2a**):

This complex was prepared by the reported method.[3)]

[Cu(hfac)$_2$(5-Hphpz)$_4$] (2b) and [Cu(hfac)$_2$(4,5-Hmppz)$_4$] (2c): These complexes were prepared by a similar method as reported for **2a**.[3)]

[Cu(hfac)$_2$(5-Hphpz)$_4$]: IR 3209(br) (N–H) and 1654 (C–O) cm^{-1}; Found: C, 53.09; H, 3.13; N, 10.64%. Calcd for $C_{46}H_{34}N_8O_4F_{12}Cu$: C, 52.40; H, 3.25; N, 10.63%.

[Cu(hfac)$_2$(4,5-Hmppz)$_4$]: IR 3209(br) (N–H) and 1661, 1650 (C–O) cm^{-1}; Found: C, 53.90; H, 3.57; N, 10.02%. Calcd for $C_{50}H_{42}N_8O_4F_{12}Cu$: C, 54.08; H, 3.81; N, 10.09%.

[Cu(tfa)$_2$(5-Hmpz)$_4$] (1a) and [Cu(tfa)$_2$(5-Hphpz)$_4$] (1b): The adduct **2a** or **2b** was decomposed on standing in petroleum ether for a few weeks, and **1a** or **1b** was obtained.

[Cu(tfa)$_2$(5-Hmpz)$_4$]: Found: C, 38.86; H, 3.86; N, 18.08%. Calcd for $C_{20}H_{24}N_8O_4F_6Cu$: C, 38.87; H, 3.91; N, 18.13%.

[Cu(tfa)$_2$(5-Hphpz)$_4$]: Found: C, 55.01; H, 3.28; N, 13.17%. Calcd for $C_{40}H_{32}N_8O_4F_6Cu$: C, 55.46; H, 3.72; N, 12.94%.

[Cu(tfa)$_2$(4-Hmpz)$_4$] (1e): [Cu(hfac)$_2$] was dissolved in petroleum ether containing a small portion of acetone with four times molar quantities of 4-methyl-1*H*-pyrazole. The solution was boiled under reflux for 1 h. After the solvent was evaporated at room temperature, a residue was obtained. After crystallization from petroleum ether, bluish violet crystals were formed. They were filtrated and dried in vacuo.

[Cu(tfa)$_2$(4-Hmpz)$_4$]: Found: C, 39.11; H, 3.94; N, 18.01; F, 18.54%. Calcd for $C_{20}H_{24}N_8O_4F_6Cu$: C, 38.87; H, 3.91; N, 18.13; F, 18.45%.

[Cu(tfa)$_2$(5-Htpz)$_4$] (1f) and [Cu(tfa)$_2$(Hpz)$_4$] (1g): These complexes were prepared by a similar method as described above.

[Cu(tfa)$_2$(5-Htpz)$_4$]: Found: C, 43.72; H, 2.63; N, 12.27%. Calcd for $C_{32}H_{24}N_8O_4S_4F_6Cu$: C, 43.17; H, 2.72; N, 12.58%.

[Cu(tfa)$_2$(Hpz)$_4$]: Found: C, 34.28; H, 2.67; N, 19.42%. Calcd for $C_{16}H_{16}N_8O_4F_6Cu$: C, 34.20; H, 2.87; N, 19.94%.

[Cu(tfa)$_2$(4,5-Hmppz)$_4$] (1c): [Cu(tfa)$_2$(4-Hmpz)$_4$] was dissolved in an acetone–water mixture with four times molar quantities of 3-methyl-4-phenyl-1*H*-pyrazole. The solution was boiled under reflux for 1 h. After standing for a few days, dark blue crystals were formed and dried in vacuo.

[Cu(tfa)$_2$(4,5-Hmppz)$_4$]: Found: C, 57.43; H, 4.34; N, 11.99%. Calcd for $C_{44}H_{40}N_8O_4F_6Cu$: C, 57.30; H, 4.37; N, 12.15%.

[Cu(hfac)$_2$(4-Hmpz)$_2$(5-Hmpz)$_2$] (2d) and [Cu(tfa)$_2$(4-Hmpz)$_2$(5-Hmpz)$_2$] (1d): [Cu(hfac)$_2$(4-Hmpz)$_2$] was prepared by the reported method.[4)] [Cu(hfac)$_2$(4-Hmpz)$_2$] was dissolved in petroleum ether with twice molar quantities of 3-methyl-1*H*-pyrazole. The solution was boiled under reflux for 1 h. After standing for several days, a bluish violet precipitate was formed and dried in vacuo.

[Cu(hfac)$_2$(4-Hmpz)$_2$(5-Hmpz)$_2$]: IR 3439, 3209(br) (N–H) and 1668, 1653 (C–O) cm^{-1}; Found: C, 38.61; H, 3.14; N, 13.75%. Calcd for $C_{26}H_{26}N_8O_4F_{12}Cu$: C, 38.74; H, 3.25; N, 13.90%.

1d was prepared from **2d** by a similar method as described for **1a**.

[Cu(tfa)$_2$(4-Hmpz)$_2$(5-Hmpz)$_2$]: Found: C, 38.98; H, 3.86; N, 18.09%. Calcd for $C_{20}H_{24}N_8O_4F_6Cu$: C, 38.87; H, 3.91; N, 18.13%.

Spectral Measurements. IR spectra were recorded on a Nicolet 5ZDX Fourier transform infrared spectrometer and the diffuse reflectance spectra on a JASCO U-Best 55 spectrophotometer.

Crystal Structure Analysis for 1e. The X-ray diffraction data were collected by use of an automated four-circle diffractometer, Rigaku AFC-5, with a graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) up to 2θ=60°, the θ–2θ scan technique being employed. The diffraction intensities were monitored by five standard reflections for every 50 reflections recorded. No signs of decomposition of the crystal were observed. The usual corrections for Lorentz and polarization effects were made with the crystal, but no absorption correction was applied. Independent reflections with $|F_o|>2.5\sigma(|F_o|)$, 2935 reflections, were used for the structure determinations. Calculations were carried out on a FACOM M-760 computer at the Rikkyo University Computer Center using the UNICS-III[17)] and ORTEP Programs.[18)] The atomic-scattering factors including the anomalous scattering factors were taken from Ref. 19 for non-hydrogen atoms and from Ref. 20 for hydrogen atom. The structure was solved by the heavy atom method, and refined by standard Patterson, Fourier, and block-diagonal least-squares techniques. The positions of all hydrogen atoms were determined from the difference Fourier map.

Crystallographic Data: $C_{20}H_{24}F_6N_8O_4Cu$, M=618.00, Triclinic, $P\bar{1}$, a=9.600(2), b=10.666(3), c=8.703(2) Å, α=115.52(2), β=113.58(2), γ=59.71(1)°, V=675.0(3) Å^3, Z=1, D_c=1.520 Mg m^{-3}, Crystal size=0.35×0.20×0.16 mm^3, $F(000)$=315, μ(Mo $K\alpha$)=8.9 cm^{-1}. The final discrepancy factors were R=0.048, and R_w=0.047 ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/|\sigma(F)|^2$). Extremes in difference Fourier are 0.52 and −0.49 eÅ^{-3}.

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9) [Cu(μ-3-mpz)$_2$]: λ_{max} 684 nm; IR no N–H; Found: C, 42.52; H, 4.37; N, 24.95%. Calcd for $C_8H_{10}N_4Cu$: C, 42.57; H, 4.47; N, 24.82%.

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