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Structures and Spectral Properties of Some Bis(β-diketonato)copper(II)-Diazole Complexes. I. The 1 : 4 and 1 : 1 Adducts of Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) and 3-Methyl-1*H*-pyrazole

Tamizo Kogane,* Minoru Ishii,†,†† Kazumasa Harada,† Reiko Hirota,† and Masayoshi Nakahara†
Industrial Research Institute of Kanagawa Prefecture, Showa-machi, Kanazawa-ku, Yokohama 236
†Department of Chemistry, Faculty of Science, Rikkyo University, Nishi-ikebukuro, Toshima-ku, Tokyo 171

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Cu(hfac)$_2$(5-Hmpz)$_4$ (**1**) and Cu(hfac)$_2$(5-Hmpz) (**2**) (Hhfac=1,1,1,5,5,5-hexafluoro-2,4-pentanedione; 5-Hmpz=5-methyl-1*H*-pyrazole) have been prepared by the stoichiometric reactions of Cu(hfac)$_2$ with 3-methyl-1*H*-pyrazole in petroleum ether. The structures of **1** and **2** have been determined by X-ray analyses. Crystal data for **1**: triclinic, $P\bar{1}$, a=9.531(1), b=10.286(2), c=8.891(2) Å, α=95.85(2), β=95.52(2), γ=85.41(1)°, V=860.9(3) Å^3, Z=1, and R=0.061. Crystal data for **2**: triclinic, $P\bar{1}$, a=9.647(6), b=12.075(9), c=9.130(5) Å, α=107.43(5), β=99.30(5), γ=87.20(6)°, V=1001.3(12) Å^3, Z=2, and R=0.064. In **1**, the geometry about each copper atom is approximately that of a tetragonal bipyramid, with four nitrogen atoms from 5-Hmpz molecules in the equatorial plane and two oxygen atoms from each hfac ligand in the axial positions. Each of the uncoordinated oxygen atoms of hfac ligands is intramolecularly hydrogen-bonded with two imino groups of adjacent 5-Hmpz molecules. In IR spectra, the split bands of $\nu_{\mathrm{C-O}}$ were observed at 1648 and 1659 cm^{-1}. In **2**, each copper atom is approximately in an environment of a tetragonal pyramid, with an oxygen atom from a hfac ligand at the apex and a nitrogen atom from a 5-Hmpz molecule in the basal plane. The copper atom is located slightly above the plane. The split bands of $\nu_{\mathrm{C-O}}$ were observed at 1644, 1662, 1669 cm^{-1}. An interpretation of the observed IR spectral bands is proposed.

Diazoles have both a pyridine-type nitrogen and a pyrrole-type nitrogen (imino group) in the same molecule, and they can react bifunctionally with many metal ions or Lewis acids giving a variety of products.[1,2] We have reported that the reaction of bis(nonfluorinated β-diketonato)copper(II) with diazoles gave diazole adducts and/or μ-diazolato complexes.[3] However, the reactions of diazoles with bis(fluorinated β-diketonato)copper(II) have scarcely been investigated. It is well known that bis(fluorinated β-diketonato)copper(II) is a strong Lewis acid and reacts with unidentate nitrogen heterocycles, e.g., pyridine, substituted pyridines, quinoline, etc., producing 1 : 1 and/or 1 : 2 adducts.[4] However, the structures of these adducts have not been fully elucidated. For several adducts of Cu(hfac)$_2$ with bidentate ligands having nitrogen donors, X-ray analyses have been made. For example, adducts with 2,2′-bipyridine (bpy),[5] 1,4-diazabicyclo[2.2.2]octane (ted),[6] pyrazine (pyz),[7] 1,8-bis(dimethylamino)naphthalene,[8] and *N*,*N*-dimethylethylenediamine (dmed)[9] have been isolated and their structures determined. It has been observed that, of these adducts, only the last one cited above, Cu(hfac)$_2$(dmed)$_2$, contains unidentate hfac ligands. We have prepared the 1 : 4 and 1 : 1 adducts of Cu(hfac)$_2$ with 3-methyl-1*H*-pyrazole and here we discuss their structures in relation to the hydrogen bonds and spectral properties.

Experimental

Materials. Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) was prepared by the reported method.[10] 3-Methyl-1*H*-pyrazole (Tokyo Kasei) was used without further purification.

Preparation of the Complexes. Cu(hfac)$_2$(5-Hmpz)$_4$: Cu(hfac)$_2$ was warmed with four times molar quantities of 3-methyl-1*H*-pyrazole in petroleum ether under reflux for 1 h. After standing for several days, violet crystals were formed and dried in vacuo. Found: C, 38.56; H, 3.19; N, 13.93; Cu, 7.84%. Calcd for $C_{26}H_{26}N_8O_4F_{12}Cu$: C, 38.74; H, 3.25; N, 13.90; Cu, 7.88%.

Cu(hfac)$_2$(5-Hmpz): Cu(hfac)$_2$ was warmed with an equimolar quantity of 3-methyl-1*H*-pyrazole in petroleum ether under reflux for 1 h. After cooling, a green precipitate was formed. It was filtered and recrystallized from petroleum ether. Found: C, 30.14; H, 1.46; N, 4.86%. Calcd for $C_{14}H_8N_2O_4F_{12}Cu$: C, 30.04; H, 1.44; N, 5.00%.

Spectral Measurement. IR spectra were recorded on a Hitachi Model 225 grating infrared spectrophotometer.

Crystal Structure Analysis. Lattice constants were first approximately determined from Weissenberg photographs obtained with Cu*Kα* radiation. Crystallographic data of both adducts are listed in Table 1. The X-ray diffraction data were collected by use of an automated four-circle diffractometer, Rigaku AFC-5, with a graphite-monochromated Mo*Kα* 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 crystals were observed. The usual corrections for Lorentz and polarization effects were made with both crystals, but no absorption correction was applied. Independent reflections with $|F_o|>3\sigma(|F_o|)$, 2173 and 2915 reflections for **1** and **2**, respectively, were used for the structure determinations. Calculations were carried out on a FACOM M-360 computer at the Rikkyo University Computer Center using the UNICS-III[11] and ORTEP Programs.[12] The atomic-scattering factors including the

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†† Present address: Chemistry Laboratory, Faculty of Education, Yamagata University, Koshirakawa, Yamagata 990.

Table 1. Crystallographic Data and Experimental Details

	1	**2**
Formula	$CuC_{26}H_{26}F_{12}N_8O_4$	$CuC_{14}H_8F_{12}N_2O_4$
M	806.07	559.76
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	9.531(1)	9.647(6)
b/Å	10.286(2)	12.075(9)
c/Å	8.891(2)	9.130(5)
α/°	95.85(2)	107.43(5)
β/°	95.52(2)	99.30(5)
γ/°	85.41(1)	87.20(6)
U/Å^3	860.9(3)	1001.3(12)
Z	1	2
D_m/Mg m^{-3}	1.55	1.84
D_c/Mg m^{-3}	1.554	1.856
Crystal size/mm	0.5×0.3×0.25	0.5×0.45×0.4
F(000)	407	550
μ(Mo $K\alpha$)/cm^{-1}	7.4	12.2
Scan rate/° min^{-1}	6	6
Scan range (2θ)/°	2—60	2—60
No. of reflection measured	4471	6226
No. of unique data used for calc. $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	2173	2915
R[a)]	0.061	0.064

a) $R = \sum \lvert \lvert F_o\rvert - \lvert F_c\rvert \rvert / \sum \lvert F_o\rvert$ (unit weight).

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

Atom	x	y	z	B_{eq}/Å^2
Cu	0	0	0	4.1
O(1)	−1198(5)	−2199(4)	6(5)	6.2
O(2)	−2666(5)	−2012(4)	2691(5)	7.2
N(1)	431(5)	−1408(4)	2783(5)	5.0
N(2)	598(5)	−301(4)	2173(5)	4.6
N(3)	−2744(5)	329(4)	1318(5)	4.5
N(4)	−1830(4)	870(4)	548(5)	4.4
C(1)	−1479(7)	−4092(6)	−1622(7)	6.1
C(2)	−1756(6)	−3228(5)	−168(6)	4.6
C(3)	−2648(6)	−3734(5)	748(7)	5.2
C(4)	−3028(6)	−3073(6)	2101(7)	5.3
C(5)	−4021(9)	−3726(8)	2996(9)	8.5
C(6)	1460(6)	359(6)	3162(7)	5.3
C(7)	1860(7)	−316(7)	4399(7)	5.9
C(8)	1189(7)	−1459(6)	4134(6)	5.2
C(9)	1208(10)	−2592(7)	5046(8)	8.8
C(10)	−2448(7)	2016(6)	280(8)	6.4
C(11)	−3712(7)	2224(7)	882(9)	7.0
C(12)	−3899(6)	1123(6)	1542(7)	5.2
C(13)	−5060(7)	724(9)	2389(9)	8.2
F(1)	−1568(7)	−5317(4)	−1608(6)	12.5
F(2)	−2274(7)	−3725(6)	−2758(5)	13.7
F(3)	−213(6)	−3990(6)	−2019(7)	13.0
F(4)	−4743(10)	−2985(6)	3791(11)	22.9
F(5)	−4857(7)	−4469(7)	2201(7)	16.1
F(6)	−3362(9)	−4544(9)	3800(10)	21.3
H(N1)	−19(6)	−190(5)	238(6)	7(2)[a)]
H(N3)	−261(5)	−46(4)	151(5)	4(1)[a)]

a) Isotropic temperature factor.

anomalous scattering factors were taken from Ref. 13 for nonhydrogen atoms and from Ref. 14 for hydrogen atom. The structures were solved by the heavy atom method, and refined by standard Patterson, Fourier, and block-diagonal least-squares techniques. The CF$_3$ groups are rotationally disordered about the C-C bonds. The greater uncertainty is reflected in the higher standard deviations for F(4) and F(6) in **1** and for F(2) and F(3) in **2**. The final R values were 0.061 for **1** and 0.064 for 2, respectively. The positions of all hydrogen atoms were determined from the difference Fourier map. The final atomic coordinates of both complexes are given in Tables 2 and 3, and the geometries of the metal coordination spheres in Tables 4 and 5.[15)]

Results and Discussion

ORTEP projections of **1** are shown in Figs. 1a and 1b with the atomic numbering. The molecule has a center of symmetry. A copper atom lies in the center of a tetragonally distorted octahedron and is coordinated with the four nitrogen atoms from 5-Hmpz molecules in the equatorial plane and by two oxygen atoms from different hfac ligands in the axial positions.

Table 3. Final Atomic Coordinates (×10^4), with Estimated Standard Deviations in Parentheses, and Their Equivalent Isotropic Temperature Factors, for **2**

Atom	x	y	z	B_{eq}/Å^2
Cu	−8(1)	1617(1)	1409(1)	4.6
O(1)	1819(4)	1408(4)	2543(5)	5.4
O(2)	755(4)	2794(4)	683(5)	5.6
O(3)	−1742(4)	1619(4)	−26(4)	5.3
O(4)	−897(4)	3015(4)	3158(4)	5.4
N(1)	159(5)	−396(4)	2613(6)	4.9
N(2)	−670(5)	259(4)	1884(6)	4.9
C(1)	4100(7)	1737(7)	3846(10)	7.5
C(2)	2875(6)	2037(5)	2760(7)	4.6
C(3)	3020(6)	2928(6)	2165(8)	5.3
C(4)	1943(6)	3226(5)	1156(7)	5.0
C(5)	2189(8)	4231(7)	527(9)	6.8
C(6)	−3793(7)	2176(7)	−1301(9)	7.5
C(7)	−2685(6)	2386(5)	144(7)	4.7
C(8)	−2857(6)	3306(5)	1384(7)	5.2
C(9)	−1956(6)	3543(5)	2822(7)	4.9
C(10)	−2354(8)	4573(6)	4112(8)	6.8
C(11)	−1956(7)	−79(7)	1876(9)	6.5
C(12)	−1925(8)	−925(7)	2596(9)	7.1
C(13)	−545(7)	−1126(5)	3044(7)	5.2
C(14)	145(9)	−1965(7)	3826(9)	7.2
F(1)	3940(6)	924(6)	4326(9)	14.6
F(2)	5160(6)	1466(10)	3258(11)	21.3
F(3)	4493(10)	2540(6)	4946(10)	25.3
F(4)	1460(6)	5134(4)	1116(7)	10.8
F(5)	3481(5)	4587(5)	877(8)	12.4
F(6)	1870(8)	3969(5)	−941(6)	13.9
F(7)	−3307(5)	1783(6)	−2560(5)	12.4
F(8)	−4634(6)	3014(5)	−1342(6)	13.2
F(9)	−4629(6)	1341(6)	−1301(7)	13.6
F(10)	−1800(8)	5505(5)	4125(8)	14.7
F(11)	−3636(6)	4792(6)	4062(8)	16.2
F(12)	−1918(10)	4498(6)	5433(6)	17.9

Table 4. Selected Bond Lengths and Bond Angles around the Copper Atom, with Estimated Standard Deviations in Parentheses, for **1**

Bond length (l/Å)		Bond angle (ϕ/°)			
Cu-O(1)	2.615(4)	Cu-O(1)-C(2)	172.6(4)	O(1)-Cu-N(2)	83.0(2)
Cu-N(2)	2.008(5)	O(1)-Cu-N(4)	85.9(2)	N(2)-Cu-N(4)	91.6(2)
Cu-N(4)	1.976(4)	Cu-N(2)-N(1)	124.0(4)	Cu-N(2)-C(6)	128.9(4)
		Cu-N(4)-N(3)	124.2(3)	Cu-N(4)-C(10)	131.4(4)

Table 5. Selected Bond Lengths and Bond Angles around the Copper Atom, with Estimated Standard Deviations in Parentheses, for **2**

Bond length (l/Å)		Bond angle (ϕ/°)			
Cu-O(1)	1.941(5)	O(1)-Cu-O(2)	90.9(2)	O(1)-Cu-O(3)	170.2(2)
Cu-O(2)	1.956(5)	O(1)-Cu-O(4)	101.4(2)	O(2)-Cu-O(3)	89.1(2)
Cu-O(3)	1.951(4)	O(2)-Cu-O(4)	88.9(2)	O(3)-Cu-O(4)	88.4(2)
Cu-O(4)	2.196(5)	N(2)-Cu-O(1)	88.1(2)	N(2)-Cu-O(2)	171.5(2)
Cu-N(2)	1.975(5)	N(2)-Cu-O(3)	90.5(2)	N(2)-Cu-O(4)	99.6(2)
		Cu-N(2)-N(1)	124.0(4)	Cu-N(2)-C(11)	130.8(5)

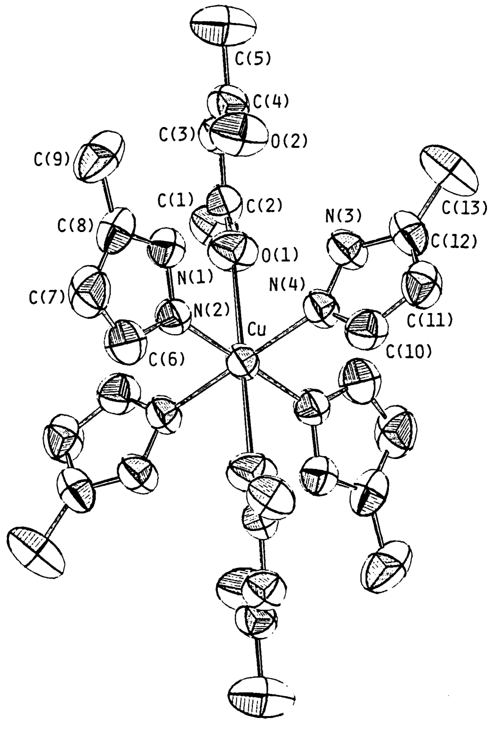

Fig. 1a. A perspective drawing of the structure of **1**, showing the numbering scheme of the atoms (50% probability thermal ellipsoids). Unlabeled atoms are related to labeled atoms by the inversion center. Fluorine atoms attached to C(1) and C(5) are omitted for clarity.

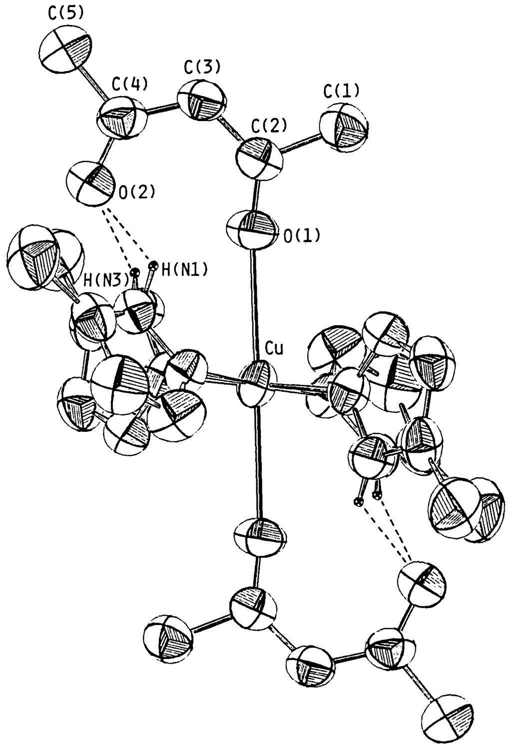

Fig. 1b. A perspective drawing of the molecular structure of **1**, showing the intramolecular hydrogen bonds. Only the H(N1) and H(N3) hydrogen atoms are shown.

The basic structure of **1** is rather similar to that of Cu(hfac)$_2$(dmed)$_2$, which also has a coordination of a tetragonal pyramid, with four nitrogen atoms in the equatorial plane and two oxygen atoms from unidentate hfac ligands at the apexes.

Another well-defined adduct with unidentate hfac ligand is Cu(acac)(hfac)(phen) (Hacac=2,4-pentanedione, phen=1,10-phenanthroline), which is five-coordinated, however, and an oxygen atom of hfac ligand is in the apical position of a tetragonal pyramid, the basal positions being occupied with two nitrogen atoms from a phen molecule and two oxygen atoms from an acac ligand.16)

The 3-methyl-1*H*-pyrazole used as a starting material is found in the form of 5-Hmpz in the adduct, which is also the case with [Cu$_2$F$_2$(3,5-Hdmpz)$_4$(5-Hmpz)$_2$](BF$_4$)$_2$17) (3,5-Hdmpz=3,5-dimethyl-1*H*-pyrazole). The 5-substituted form may be more favorable than the other tautomer, probably because

Table 6. Selected Bond Lengths of hfac's Ligands and around the Copper Atom in Nitrogen Base Adducts

Complex	Bond length (l/Å) C(2)-C(3) (C(7)-C(8)	C(3)-C(4) C(8)-C(9)	C(2)-O(1) C(7)-O(3)	C(4)-O(2) C(9)-O(4))	Cu-O(1) (Zn-O(1))	Cu-O(2) (Zn-O(2))	Cu-O(3)	Cu-O(4)	Cu-N(1) (Zn-N(1))	Cu-N(2)
Six coordinated										
Cu(hfac)$_2$(ted)[6]	1.378(9)	1.382(9)	1.247(8)	1.262(7)	1.958(5)	1.954(5)			2.566(7)	
Cu(hfac)$_2$(py)$_2$[18]	1.386(14)	1.378(13)	1.24(1)	1.257(11)	2.266(6)	2.002(6)			2.003(6)	2.021(7)
	1.418(13)	1.353(15)	1.238(10)	1.263(10)			2.300(6)	1.994(5)		
Zn(hfac)$_2$(py)$_2$[18]	1.407(19)	1.359(17)	1.249(15)	1.288(14)	2.159(7)	2.069(8)			2.116(7)	
Cu(hfac)$_2$(pyz)[7]	1.38(1)	1.37(1)	1.25(1)	1.27(1)	2.004(7)	1.924(7)			2.529(9)	
Unidentate hfac's										
Adduct **1**	1.395(8)	1.385(9)	1.212(7)	1.222(8)	2.615(4)				2.008(5)	1.976(4)
Cu(hfac)$_2$(dmed)$_2$[9]	1.385(5)	1.395(4)	1.235(4)	1.233(4)	2.793(2)				1.989(3)	2.064(3)
Five coordinated										
Adduct **2** ring 1	1.364(9)	1.383(9)	1.254(8)	1.239(8)	1.941(5)	1.956(5)			1.975(5)	
ring 2	1.354(9)	1.412(9)	1.259(8)	1.223(8)			1.951(4)	2.196(5)		
[Cu(hfac)$_2$]$_2$(pyz)[7]	1.39(3)	1.37(3)	1.24(2)	1.26(2)	1.96(1)	1.93(1)			2.25(2)	
	1.39(2)	1.36(2)	1.26(2)	1.22(2)						
Unidentate hfac's										
Cu(acac)(hfac)(phen)[16]	1.395(11)	1.410(12)	1.235(9)	1.224(10)	1.901(5)	1.912(5)	2.341(5)		2.014(5)	2.015(6)

of the less steric crowding around the coordinating site.

Table 4 contains the selected bond lengths and bond angles in **1**. Also in Table 6, the bond lengths and bond angles of several adducts of bis(β-diketonato)-copper(II) in the literatures are summarized for comparison.

The Cu-O(1) distance (2.615(4) Å) is considerably longer than the corresponding Cu-O distances found in bis(2,4-pentanedionato)copper(II) or its adducts. For example, the average Cu-O bond lengths in planar Cu(hfac)$_2$ and cis-octahedral Cu(hfac)$_2$(py)$_2$[18] are 1.989(14) and 2.283(12) Å, respectively. In the case of the adducts containing unidentate hfac ligands, a comparably long Cu-O distance of 2.793(2) Å, and a some shorter Cu-O distance of 2.341(5) Å have been observed in Cu(hfac)$_2$(dmed)$_2$ and Cu(acac)(hfac)(phen), respectively.

The hfac ligand is planar and has an approximate C_2 symmetry axis. The C(2)-O(1) and C(4)-O(2) distances are similar, i.e., 1.212(7) and 1.222(8) Å, respectively, and the C(2)-C(3) and C(3)-C(4) distances have nearly the same values of 1.395(8) and 1.385(9) Å, respectively.

These data suggest the complete delocalization of π-electrons in the hfac chelate ring. The C-O and C-C distances agree with the corresponding bond lengths in Cu(hfac)$_2$(dmed)$_2$ and Cu(acac)(hfac)(phen), and it has been discussed that these two adducts also have delocalized hfac rings.

As shown in Figs. 1a and 1b, the geometry of the unidentate hfac ligand in the molecule is unique in that Cu-O(1)-C(2) bond angle is exceptionally large (172.6(4)°), which is only comparable with the corresponding angle of 166.7(2)° in Cu(hfac)$_2$(dmed)$_2$. It is also of interest that the C_2 symmetry axis of hfac ligand is not perpendicular to the CuN$_4$ plane but is rather slanted against it, so that the coordinated O(1) atom lies nearer to the plane than the uncoordinated O(2) atom. The distances from the CuN$_4$ plane to O(1) and O(2) are 2.588(5) and 3.050(7) Å, respectively, while the Cu-O(2) distance is 4.414(5) Å. It may be reasonable that both in **1** and Cu(hfac)$_2$(dmed)$_2$, the geometry of the hfac ligands is stabilized by intramolecular hydrogen bonding. In Cu(hfac)$_2$(dmed)$_2$, the distances of the uncoordinated oxygen atom from the copper atom and from a NH$_2$-nitrogen atom of a dmed ligand are 4.226 Å and 2.995(3) Å, respectively. These values suggest that the uncoordinated oxygen atoms have no interaction with the copper atom and are intramolecularly hydrogen-bonded to the N atoms of the chelated dmed molecules.

Table 7. Distances O···N (l/Å) and Angles (ϕ/°) O···H-N of Hydrogen Bonds for **1**

O···N		O···H-N	
O(1)···N(3)	3.065(6)	O(1)···H(N3)-N(3)	125(4)
O(1)···N(1)	2.867(6)	O(1)···H(N1)-N(1)	132(5)
O(2)···N(3)	2.802(7)	O(2)···H(N3)-N(3)	157(4)
O(2)···N(1)	3.056(7)	O(2)···H(N1)-N(1)	133(5)

The data of several interactions between oxygen atoms and imino groups in **1** are summarized in Table 7. In Fig. 1b a perspective drawing of the structure of **1** is shown, indicating the hydrogen bonds. The uncoordinated oxygen atom forms intramolecular hydrogen bonds with adjacent two imino groups of the 5-Hmpz molecules. One bond is O(2)···H(N3)-N(3) and the other, probably a weaker one, is O(2)···H(N1)-N(1). In addition, it may be possible that a very weak hydrogen bond O(1)···H(N1)-N(1) is formed between the coordinated hfac oxygen atom and an imino group. The rather short distance of O(1)-H(N1) may favor the bond formation.

The Cu–N bond lengths have usual values, but it is interesting that the distances of adjacent Cu–N are not equal. Thus for Cu–N(2) and Cu–N(4), the bond lengths are 2.008(5) and 1.976(4) Å, respectively.

The planes of the coordinated 5-Hmpz molecules are slanted against the equatorial plane, so that the two imino groups are favorably located to form hydrogen bonds with an adjacent oxygen atom. The dihedral angle between the planes of the two adjacent 5-Hmpz molecules is 78.4°.

An ORTEP projection of adduct **2** is shown in Fig. 2. The molecule contains a five-coordinated copper ion, coordinated with two bidentate hfac ligands and a 5-Hmpz molecule.

The geometry is that of a tetragonal pyramid with an oxygen atom from a hfac ligand at the apex and nitrogen atom from a 5-Hmpz molecule in the basal plane. The copper atom is above the basal plane by 0.157(2) Å. This structure is similar to that of Cu(acac)$_2$(4-ampy) (4-ampy=4-aminopyridine), which is the only 1 : 1 adduct of bis(β-diketonato)copper(II) so far investigated by X-ray analysis.19)

Table 5 contains the selected bond lengths and bond angles of **2**. The apical Cu–O(4) distance (2.196(5) Å) is greater than the basal Cu–O distances, the mean value of which is 1.950(12) Å. These values are comparable with the corresponding values of Cu(acac)$_2$(4-ampy).

Of the two hfac chelate rings, the one almost in the basal plane (ring 1) is different from the other (ring 2). In the ring 1, C(2)–C(3) and C(3)–C(4) distances as well as C(2)–O(1) and C(4)–O(2) distances are similar to each other. On the other hand, the other hfac chelate ring (ring 2) is distorted. The C(7)–C(8) and C(8)–C(9) distances are different from each other and so are the C(7)–O(3) and C(9)–O(4) distances. The alternation of long and short bond lengths in the β-diketonato chelate rings has been observed in the cis-octahedral adducts of Cu(hfac)$_2$(py)$_2$ and Cu(hfac)$_2$(bpy). It has not been fully established that these facts may suggest the presence of a partially localized structure of hfac ligands.

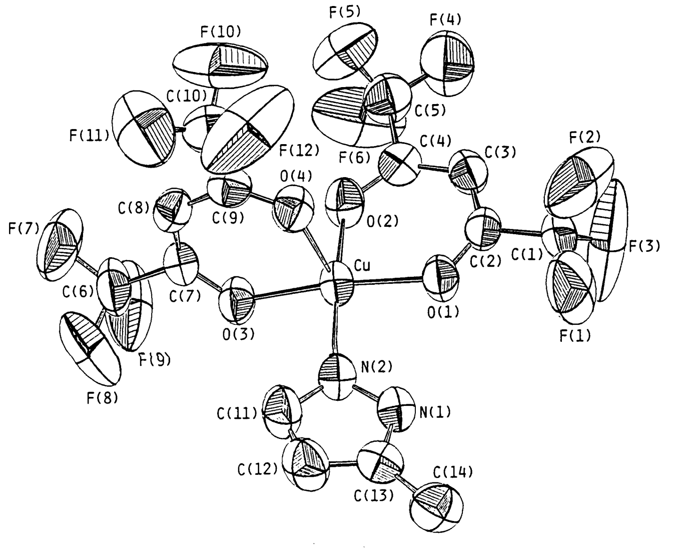

Fig. 2. A perspective drawing of the structure of **2**, showing the numbering scheme of the atoms (50% probability thermal ellipsoids).

The hfac rings are planar and dihedral angle of each hfac plane against O$_3$N plane is 1.53° and 78.2°. The angle between the two hfac planes is 76.8°.

Although the adducts **1** and **2** were prepared by stoichiometric reactions of Cu(hfac)$_2$ and 3-methyl-1*H*-pyrazole, the 1 : 2 adduct was not obtained by the similar method. The adduct **1** loses three molecules of 3-methyl-1*H*-pyrazole on standing for several weeks in the atmosphere, yielding **2**. This change may correspond to the bond formation by the uncoordinated carbonyls in **1**, displacing the 5-Hmpz molecules.

In Table 8, IR spectral data of **1** and **2** are listed. In general, the adduct formation of Cu(hfac)$_2$ and Cu(tfac)$_2$ (Htfac=1,1,1-trifluoro-2,4-pentanedione) weakens the Cu–O bonds, as evidenced by the shifts of the carbonyl stretching bands to the higher-frequency side from those observed for the parent complexes.6,16,18,20)

Attempts have also been made to correlate the C–O bond lengths of the adducts to the $\nu_{\text{C-O}}$ frequencies at about 1650 cm^{-1} of IR spectra.18) However, the approach to the bond types of the adducts by this way has not been fully attained.

The sharp band at 3424 cm^{-1} of **2** is definitely assignable to $\nu_{\text{N-H}}$ vibration of a free imino group. There is no interaction of hydrogen bonding, as it has been reported that, on making a hydrogen bond, the $\nu_{\text{N-H}}$ band shifts to lower-frequency side and line broadening occurs.21) The O(1)–N(1) distance of 2.788(7) Å and O(1)···H(N1)–N(1) angle of 118(5)° may not be favorable for formation of a hydrogen bond. On the other hand, the spectrum of **1** has two broad bands in this region at 3270 cm^{-1} and at about 3200 cm^{-1}. Therefore these bands of **1** are assigned to the $\nu_{\text{N-H}}$ vibration of hydrogen-bonded imino groups.

The split $\nu_{\text{N-H}}$ bands may be indicative of the two different N–H···O hydrogen bonds described above.

Two separate bands with approximately equal intensities are observed in the IR spectrum of **1** at 1648 and 1659 cm^{-1}, which may be assigned to the $\nu_{\text{C-O}}$ vibrations of the coordinated and uncoordinated carbonyl groups, respectively.

Table 8. IR Spectral Data

Assignment	Adduct 1	Adduct 2	Cu(hfac)$_2$22)
$\nu_{\text{N-H}}$/cm^{-1}	3270(m)	3424(m)	
	ca. 3200(m, br)		
$\nu_{\text{C-O}}$/cm^{-1}		1669(m)	
	1659(s)	1662(m)	
	1648(s)	1644(s)	1644(s)
		1615(w)	1614(w)
		1607(w)	

On the other hand, the spectra of **2** have three bands in carbonyl region at 1644, 1662, and 1669 cm^{-1} with approximate intensities of 2 : 1 : 1, respectively. For the adducts of bis(β-diketonato)metal(II) complexes, the splitting of a $\nu_{\text{C-O}}$ band in IR spectra has been reported only in the case of cis-octahedral Zn(hfac)$_2$(py)$_2$ observed at 1645 and 1660 cm^{-1},[18] which have been assigned to the stretching vibrations of carbonyls in the chelated hfac ligands with long and short C-O distances, respectively.

Thus far no information on the splitting of $\nu_{\text{C-O}}$ bands in the spectra of bis(β-diketonato)copper(II) adducts has been given. However, if the precise data are accumulated, the IR spectra may be of diagnostic help in predicting these structures of the adducts.

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