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

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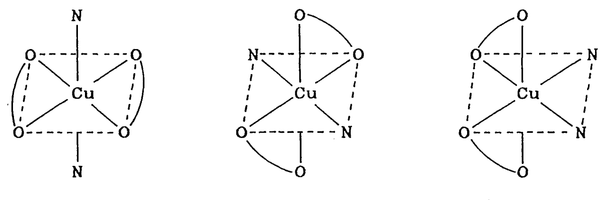
The preparation of Cu(hfac)$_2$(4-Hmpz) (**1**), Cu(hfac)$_2$(4-Hmpz)$_2$ (**2**), and Cu(hfac)$_2$(4-Hmpz)$_3$ (**3**) by stoichiometric reactions of Cu(hfac)$_2$ (Hhfac=1,1,1,5,5,5-hexafluoro-2,4-pentanedione) with 4-methyl-1*H*-pyrazole (4-Hmpz) in petroleum ether is reported. The structure of **2** has been determined by X-ray analysis. Crystal data for **2**: triclinic, $P\bar{1}$, a=9.301(3), b=10.815(2), c=6.457(1) Å, α=104.71(2), β=101.38(2), γ=75.41(2)°, V=601.8(3) Å^3, Z=1, and R=0.057. The geometry about each copper atom is approximately a tetragonal bipyramid. The axial positions are occupied by two oxygen atoms one from each of the bidentate hfac ligands, the other oxygen atoms of which are in the basal plane with two nitrogen atoms from 4-Hmpz molecules. The two nitrogen atoms are situated trans to each other. The axial oxygen atoms have a considerably long Cu-O(2) distance (2.346(3) Å). In the IR spectrum of **2**, unsplit ν C-O and ν N-H bands were observed at 1678 and 3441 cm^{-1}, respectively. The structures of **1** and **3** are estimated on the basis of their IR spectra.

The ability of bis(fluorinated β-diketonato)copper(II) complexes to behave as strong Lewis acids and to react with unidentate or bidentate nitrogen ligands to form addition complexes have been reported.[2] Particularly several X-ray investigations have been reported on the six-coordinated adducts of Cu(hfac)$_2$ with nitrogen bases. For example, Cu(hfac)$_2$ (bpy)[3] (bpy=2,2′-bipyridine) and Cu(hfac)$_2$(py)$_2$[4] (py= pyridine) have cis-N$_2$O$_2$ octahedral structure (**c**) and Cu(hfac)$_2$(ted)[5] (ted=1,4-diazabicyclo[2.2.2]octane) and Cu(hfac)$_2$(pyz)[6] (pyz=pyrazine) have O$_4$ octahedral structure (**a**). The bond lengths of Cu-O(1), Cu-O(2), and Cu-N(1) are 2.004(7), 1.924(7), and 2.529(9) Å respectively in Cu(hfac)$_2$(pyz), and 1.958(5), 1.954(5), and 2.566(7) Å respectively in Cu(hfac)$_2$(ted). These data show that the structures of these adducts exactly belong to the O$_4$ octahedral type. Trans-N$_2$O$_2$ octahedral structure (**b**) has not been reported so far and adduct **2** may be the first example with a structure assigned to this type.



(**a**) O$_4$ Oh
Cu(hfac)$_2$(pyz)
Cu(hfac)$_2$(ted)

(**b**) trans-N$_2$O$_2$ Oh

(**c**) cis-N$_2$O$_2$ Oh
Cu(hfac)$_2$(bpy)
Cu(hfac)$_2$(py)$_2$

Cu(hfac)$_2$ adduts with nitrogen heterocycles.

In this paper, we report on 1 : 1, 1 : 2, and 1 : 3 adducts of Cu(hfac)$_2$ with 4-methyl-1*H*-pyrazole and discuss the relations between the structures and spectral properties of them.

Experimental

Materials. Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) was prepared by the reported method.[7] 4-Methyl-1*H*-pyrazole, 1*H*-pyrazole (Hpz), and 4-iodo-1*H*-pyrazole (4-Hipz) (Aldrich Chemical Co.) were used without further purification.

Preparation of the Complexes. Cu(hfac)$_2$(4-Hmpz): Cu(hfac)$_2$ was dissolved in petroleum ether with an equimolar quantity of 4-methyl-1*H*-pyrazole. The solution was boiled under reflux for 1 h. On cooling, green crystals were formed. They were separated by filtration and recrystallized from petroleum ether. Found: C, 30.17; H, 1.36; N, 5.08%. Calcd for C$_{14}$H$_8$N$_2$O$_4$F$_{12}$Cu: C, 30.04; H, 1.44; N, 5.00%.

Cu(hfac)$_2$(4-Hmpz)$_2$: Cu(hfac)$_2$ was dissolved in petroleum ether with twice molar quantities of 4-methyl-1*H*-pyrazole. The solution was boiled under reflux for 1 h. After standing for a few days, light green crystals were formed. They were separated by filtration and recrystallized from petroleum ether. Found: C, 33.72; H, 2.16; N, 8.80%. Calcd for C$_{18}$H$_{14}$N$_4$O$_4$F$_{12}$Cu: C, 33.68; H, 2.20; N, 8.73%.

Cu(hfac)$_2$(4-Hmpz)$_3$: Cu(hfac)$_2$ was dissolved in petroleum ether with three times molar quantities of 4-methyl-1*H*-pyrazole. The solution was boiled under reflux for 1 h. After standing for a few days, bluish green crystals were formed. They were separated by filtration and dried in vacuo. Found: C, 36.47; H, 2.73; N, 11.57%. Calcd for C$_{22}$H$_{20}$N$_6$O$_4$F$_{12}$Cu: C, 36.50; H, 2.78; N, 11.61%.

Cu(hfac)$_2$(Hpz)$_2$ and Cu(hfac)$_2$(4-Hipz)$_2$: These complexes were prepared by a similar method as described above. Cu(hfac)$_2$(Hpz)$_2$: IR 3429 (N-H) and 1668 (C-O) cm^{-1}; Found: C, 31.36; H, 1.64; N, 8.95%. Calcd for C$_{16}$H$_{10}$N$_4$O$_4$F$_{12}$Cu: C, 31.31; H, 1.64; N, 9.13%. Cu(hfac)$_2$(4-Hipz)$_2$: IR 3418 (N-H) and 1661 (C-O) cm^{-1}; Found: C, 22.24; H, 0.77; N, 6.19%. Calcd for C$_{16}$H$_8$N$_4$O$_4$F$_{12}$I$_2$Cu: C, 22.20; H, 0.93; N, 6.47%.

Cu(hfac)$_2$(bpy)[3] and Cu(hfac)$_2$(dmed)$_2$[8] (dmed=*N*,*N*-dimethylethylenediamine) were prepared by the reported

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methods.

Spectral Measurements. The diffuse reflectance spectra were recorded on a Hitachi Model 3410 spectrophotometer and IR on a Nicolet 5ZDX Fourier transform infrared spectrometer.

Crystal Structure Analysis for 2. Crystallographic data and experimental details of the adduct 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 $K\alpha$ 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 $|F_o| > 3\sigma(|F_o|)$, 2673 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[9] and ORTEP Programs.[10] The atomic-scattering factors including the anomalous scattering factors were taken from Ref. 11 for non-hydrogen atoms and from Ref. 12 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 final R value was 0.057. The positions of all hydrogen atoms were determined from the difference Fourier map. The final atomic coordinates of the complex are given in Table 2, and the geometry of the metal coordination sphere in Table 3.[13]

Table 1. Crystallographic Data and Experimental Details

Formula	$CuC_{18}H_{14}F_{12}N_4O_4$
M	641.86
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.301(3)
b/Å	10.815(2)
c/Å	6.457(1)
α/°	104.71(2)
β/°	101.38(2)
γ/°	75.41(2)
U/Å^3	601.8(3)
Z	1
D_m/Mg m^{-3}	1.77
D_c/Mg m^{-3}	1.771
Crystal size/mm	0.45×0.35×0.30
F(000)	319
μ(Mo $K\alpha$)/cm^{-1}	10.3
Scan rate/° min^{-1}	6
Scan range (2θ)/°	2—60
No. of reflection measured	3831
No. of unique data for calc. $|F_o|>3(\sigma|F_o|)$	2673
$R^{a)}$	0.057
$R_w^{b)}$	0.054

a) $R=\sum||F_o|-|F_c||/\sum|F_o|$. b) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w=1/|\Delta F|^2$, $|\Delta F|^2=a|F_o|^2+b|F_o|+c$, where a=0.0017, b=−0.026, and c=0.46.

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

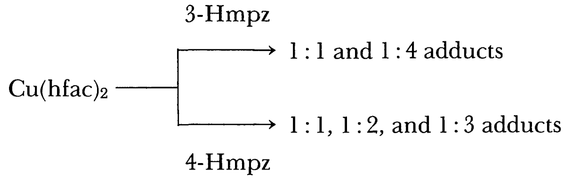
Atom	x	y	z	B_{eq}/Å^2
Cu	0	0	0	3.1
F(1)	−1884(3)	3025(3)	−4275(4)	5.5
F(2)	−997(4)	4140(3)	−1305(5)	6.6
F(3)	−3365(4)	4369(3)	−2185(6)	7.1
F(4)	−5081(5)	3078(4)	3087(9)	11.0
F(5)	−4392(5)	1318(5)	3900(8)	11.4
F(6)	−5663(4)	1500(7)	939(8)	14.4
O(1)	−827(3)	1517(2)	−1370(4)	3.7
O(2)	−2210(3)	620(3)	1582(5)	4.1
N(1)	1455(4)	762(4)	4475(6)	4.4
N(2)	938(3)	1127(3)	2580(5)	3.5
C(1)	−2083(5)	3500(4)	−2218(7)	4.3
C(2)	−1997(4)	2399(3)	−1073(5)	3.3
C(3)	−3116(5)	2503(4)	76(7)	4.1
C(4)	−3160(4)	1587(4)	1269(6)	3.6
C(5)	−4595(5)	1838(5)	2284(8)	5.1
C(6)	1148(4)	2351(4)	2969(6)	3.8
C(7)	1790(4)	2750(4)	5087(6)	3.9
C(8)	1965(5)	1704(5)	5986(7)	4.7
C(9)	2188(8)	4046(6)	6150(10)	5.7

Table 3. 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)	1.975(3)	Cu-O(1)-C(2)	129.0(3)
Cu-O(2)	2.346(3)	Cu-O(2)-C(4)	121.2(3)
Cu-N(2)	1.988(3)	O(1)-Cu-O(2)	86.1(1)
O(1)-C(2)	1.264(5)	O(1)-Cu-N(2)	90.5(1)
O(2)-C(4)	1.219(5)	O(2)-Cu-N(2)	88.3(1)
C(2)-C(3)	1.360(6)		
C(3)-C(4)	1.414(6)		

Results and Discussion

The reaction products of Cu(hfac)$_2$ with 3-methyl-1H-pyrazole (3-Hmpz) and with 4-methyl-1H-pyrazole are shown in Scheme 1. 4-Hmpz molecule gives 1 : 1, 1 : 2, and 1 : 3 adducts by the reaction (Table 4), while 3-Hmpz molecule gives 1 : 1 and 1 : 4 adducts as described in our previous paper.[1]



Scheme 1. Reaction products of Cu(hfac)$_2$ with 3-methyl-1H-pyrazole and with 4-methyl-1H-pyrazole.

As the scheme shows, the products with corresponding compositions are not always obtained when differently substituted 1H-pyrazole is used as a base in the reaction. Although 3-Hmpz and 4-Hmpz molecules have similar pK_a values of 3.3 and 3.1, respectively, 3-Hmpz molecule gives a 1 : 4 adduct rather than a 1 : 2 adduct. It is observed that still weaker bases i.e., Hpz molecule (pK_a=2.5) and 4-Hipz molecule (pK_a=0.8) also yield 1 : 2 adducts with Cu(hfac)$_2$. Probably the

Table 4. IR Spectral Data of the Adducts with Assignments

Complex	Assignment /cm^{-1}			
	ν N-H	ν C-O	ν C=C	δ_sCF$_3$
Cu(hfac)$_2$(4-Hmpz)	3396	1644 1656	1559	592 581
Cu(hfac)$_2$(4-Hmpz)$_2$	3441	1678	1552	590 578
Cu(hfac)$_2$(4-Hmpz)$_3$	3427 ca.3200(br)	1670	1557	576

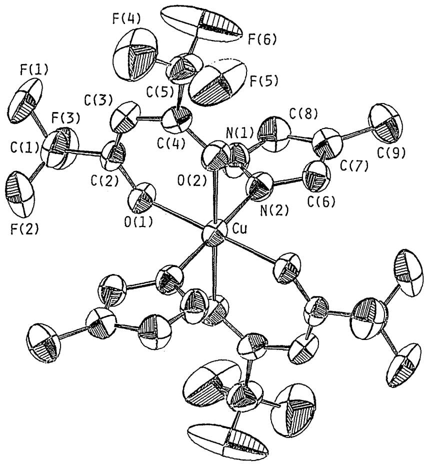


Fig. 1. A perspective drawing of the structure of **2**, showing the numbering scheme of the atoms (50% probability thermal ellipsoids).

difference in basicity between 3-Hmpz and 4-Hmpz molecules may have some effects on the reaction of adduct formation.

ORTEP projection of **2** is shown in Fig. 1 with the atomic numbering. The molecule has a center of symmetry and the geometry about each copper atom is approximately a tetragonal bipyramid. The axial positions are occupied by two oxygen atoms one from each of the bidentate hfac ligands. The other oxygen atoms of each hfac ligand are in the basal plane with two nitrogen atoms from 4-Hmpz molecules. The two nitrogen atoms are situated trans to each other. The axial oxygen atoms have a considerably long Cu-O(2) distance (2.346(3) Å), which is longer than that of equatorial Cu-O in this adduct (1.975(3) Å) and is similar to that of Cu-O between a copper atom and a unidentate hfac ligand (2.341(5) Å) in Cu(acac)(hfac)-(phen).[14] Also the axial Cu-O bond lengths in cis-N$_2$O$_2$ octahedral complexes have generally similar values. For example, in Cu(hfac)$_2$(py)$_2$[4] and Cu(hfac)$_2$-(bpy),[3] the corresponding bond lengths are 2.283(12) and 2.296 Å, respectively.

The C(2)-O(1) and C(4)-O(2) distances are different, i.e., 1.264(5) and 1.219(5) Å, respectively, and the C(2)-C(3) and C(3)-C(4) distances have also the different values of 1.360(6) and 1.414(6) Å, respectively. Different C-O and C-C distances have also been observed in one of the hfac chelate rings of Cu(hfac)$_2$(5-Hmpz).[1]

These values may suggest the delocalization of electrons in the hfac ring. In the IR spectrum, ν C-O band of **2** is observed at 1678 cm^{-1} which is higher than any other ν C-O frequencies of hfac in copper(II) complexes so far reported (Table 5). A single ν C=C band was observed at 1552 cm^{-1} and two separate bands with approximately equal intensities are observed at 590 and 578 cm^{-1}, which may be assigned to CF$_3$ deformation.[5,6,14] The former band is assignable to the CF$_3$ group attached to the carbonyl group with common Cu-O distance, while the latter to the CF$_3$ group attached to the carbonyl group with long Cu-O distance. It is to be noted that no splitting of ν C-O and νC=C bands are observed, although the different C-O and C=C distances are found in the hfac chelating ligands.

The sharp band at 3441 cm^{-1} of **2** is definitely assignable to ν N-H vibration of free imino groups which suggests that imino groups are not hydrogen-bonded.[1]

Although the structure of **1** has not been analyzed, it

Table 5. IR Spectral Data of hfac Ligands with Assignments

Complex	Nature	Assignment/cm^{-1}		
		ν C-O	ν C=C	δ_sCF$_3$
Cu(hfac)$_2$(4-Hmpz)$_2$	Trans-N$_2$O$_2$ Oh	1678	1552	590 578
[Cu(acac)(phen)(OH$_2$)][hfac]·H$_2$O[14]	Uncoordinated hfac	1673		572
Cu(hfac)$_2$(dmed)$_2$[8]	Unidentate hfac	1670		574
Cu(acac)(hfac)(phen)[14]	Unidentate hfac	1660		570
Cu(hfac)$_2$(5-Hmpz)$_4$[1]	Unidentate hfac	1663 1650	1587	576
Cu(hfac)$_2$(bpy)[2]	Cis-N$_2$O$_2$ Oh	1659	1552	586 578
Cu(hfac)$_2$(py)$_2$[4]	Cis-N$_2$O$_2$ Oh	1655		
Cu(hfac)$_2$(ted)[5]	O$_4$ Oh	1640	1558	593
Cu(hfac)$_2$(pyz)[6]	O$_4$ Oh	1639	1553	590
(tedH)$^+$(hfac)$^-$[5]	Ionic	1666		
(tmndH)$^+$(hfac)$^-$[5]	Ionic	1665		

is very likely that it has a structure similar to Cu(hfac)$_2$(5-Hmpz), which has a geometry of a tetragonal pyramid with a 5-Hmpz molecule in the basal plane. The IR spectra have some similarities between them. In **1**, two bands were observed in the carbonyl stretching region at 1644 and 1656 cm^{-1}, which may be assigned to the ν C–O vibrations of the two unequivalent hfac chelate rings. The band at 3396 cm^{-1} is assignable to ν N–H vibration. These spectral data can be comparable with those of Cu(hfac)$_2$(5-Hmpz). The spectrum of Cu(hfac)$_2$(5-Hmpz) has three bands in the carbonyl region at 1644, 1662, and 1669 cm^{-1} and a sharp band in the N–H stretching region at 3424 cm^{-1}.[1)]

In the diffuse reflectance spectrum, **1** has a broad maximum at 760 nm, while the maximum of Cu(hfac)$_2$(5-Hmpz) is observed at 793 nm (Fig. 2).

From these data of IR and UV spectra, it may be assumed that **1** has a structure similar to Cu(hfac)$_2$(5-Hmpz). It may be suggested from the IR spectrum that the axial Cu–O bond length is shorter than that of Cu(hfac)$_2$(5-Hmpz).

The preparation of **3** is rather difficult, for the formation of it sensitively depends on the reaction conditions. On recrystallization, it loses one molecule of 4-Hmpz yielding **2**. Accordingly, it is assumed that **2** and **3** are structually closely related.

The structure of **3** has not been determined owing to the difficulty in obtaining single crystals suitable for X-ray analysis. Thus we try to estimate a possible structure of **3** on the knowledge of IR and UV spectra. The relations between the coordination modes of hfac ligands and IR spectra have been discussed on Cu(hfac)$_2$ adducts. However, the spectral data have had limited use for structural determination. For example, close structural resemblance has often been expected between analogous complexes when similar spectral data are obtained for them. Recently, we have found that significant information can be obtained from spectral data and their diagnostic use for the structure determination of adducts may be very helpful. The IR spectrum of **3** has two bands in N–H stretching region at 3427 and at about 3200 cm^{-1}. The former is assigned to the N–H stretching vibration of free imino groups, and the latter to that of hydrogen-bonded imino groups. Similar broad peaks at about 3200 cm^{-1} have been observed in the spectra of Cu(hfac)$_2$(dmed)$_2$ and Cu(hfac)$_2$(5-Hmpz)$_4$, in which the presence of N–H···O hydrogen bonds has been established.

Thus, it may be safe to conclude that **3** has both free imino and N–H···O hydrogen-bonded imino groups.

The bands at 1670 and 576 cm^{-1} are assignable to ν C–O and δ_sCF$_3$, respectively. From the IR spectra of many Cu(hfac)$_2$ adducts, it can be assumed that the presence of a single ν C–O band in the range of 1638 to 1678 cm^{-1} shows the equivalence of the two hfac ligands in the complexes. For example, Cu(hfac)$_2$(5-Hmpz) has three bands in this region, as described above. On the other hand, most of the complexes with equivalent hfac's, e.g. Cu(hfac)$_2$(dmed)$_2$, Cu(hfac)$_2$(pyz), Cu(hfac)$_2$(py)$_2$ and so on, have a single band in the region. The only exception is Cu(hfac)$_2$(5-Hmpz)$_4$, which has ν C–O bands at 1650 and 1663 cm^{-1} although two unidentate hfac ligands are equivalent. These data may suggest that two hfac's are equivalent in **3**.

The frequencies of ν C–O and δ_sCF$_3$ of **3** are similar to those of Cu(hfac)$_2$(dmed)$_2$, which may suggest the similarity of the coordination mode of hfac ligands between both adducts. In Cu(hfac)$_2$(dmed)$_2$, the geometry about each copper atom is approximately a tetragonal bipyramid, with four nitrogen atoms from dmed molecules in the equatorial plane and two oxygen atoms one from each hfac ligand in the axial position. The hfac ligands are stabilized by intramolecular hydrogen bonding between uncoordinated oxygen atoms of hfac ligands and NH$_2$-nitrogen atoms of dmed ligands.

The diffuse reflectance spectrum of **3** resembles to that of **2**, showing a broad maximum at 686 nm (Fig. 2). It may suggest a similarity of the coordination

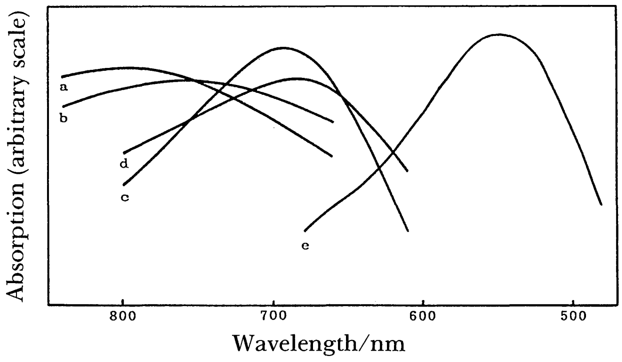


Fig. 2. The diffuse reflectance spectra of the adducts (λ_{max} (nm) in parentheses): (a) Cu(hfac)$_2$(5-Hmpz) (793), (b) Cu(hfac)$_2$(4-Hmpz) (760), (c) Cu(hfac)$_2$(4-Hmpz)$_2$ (689), (d) Cu(hfac)$_2$(4-Hmpz)$_3$ (686), and (e) Cu(hfac)$_2$(5-Hmpz)$_4$ (552).

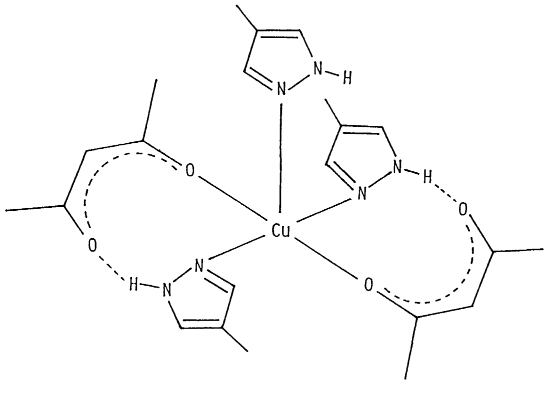


Fig. 3. The possible structure of **3** illustrated schematically.

environment around a copper atom between **2** and **3**.

In conclusion, these spectral data of **3** are consistent with the following structure. It has a geometry of a tetragonal pyramid, two nitrogen atoms from 4-Hmpz molecules and two oxygen atoms from two unidentate hfac ligands being in the basal plane. The uncoordinated oxygen atoms of hfac's are hydrogen bonded to the imino groups of 4-Hmpz molecules. The two nitrogen atoms are trans to each other. At the apex another nitrogen atom from 4-Hmpz molecule is situated. Figure 3 schematically illustrates the possible structure of **3**.

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References

1) Part I: T. Kogane, M. Ishii, K. Harada, R. Hirota, and M. Nakahara, *Bull. Chem. Soc. Jpn.*, **62**, 2524 (1989).

2) R. C. Mehrotra, R. Bohra, and D. P. Gaur, "Metal β-Diketonates and Allied Derivatives," Academic Press, London (1978), Chap. 2.

3) M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Am. Chem. Soc.*, **91**, 1859 (1969).

4) J. Pradilla-Sorzano and J. P. Fackler Jr., *Inorg. Chem.*, **12**, 1174 (1973).

5) R. C. E. Belford, D. E. Fenton, and M. R. Truter. *J. Chem. Soc., Dalton Trans.*, **1972**, 2208.

6) R. C. E. Belford, D. E. Fenton, and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, **1974**, 17.

7) J. A. Bertrand and R. I. Kaplan, *Inorg. Chem.*, **5**, 489 (1966).

8) M. A. Bush, D. E. Fenton, R. S. Nyholm, and M. R. Truter, *Chem. Commun.*, **1970**, 1335; M. A. Bush and D. E. Fenton, *J. Chem. Soc., A*, **1971**, 2446.

9) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1978).

10) C. K. Johnson, ORTEP, (1965). Report ORNL-3794, Oak Ridge National Laboratory, Tennessee.

11) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 73, 79.

12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

13) The remaining bond lengths and angles, the coordinates and isotropic temperature factors of hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and the F_o—F_c table have been deposited as Document No. 8917 at the Office of the Editor of *Bull. Chem. Soc. Jpn.*

14) N. A. Bailey, D. E. Fenton, M. V. Franklin, and M. Hall, *J. Chem. Soc., Dalton Trans.*, **1980**, 984.