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Structure and Spectral Properties of Tris[bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)]bis(μ-5-methylpyrimidine)copper(II)

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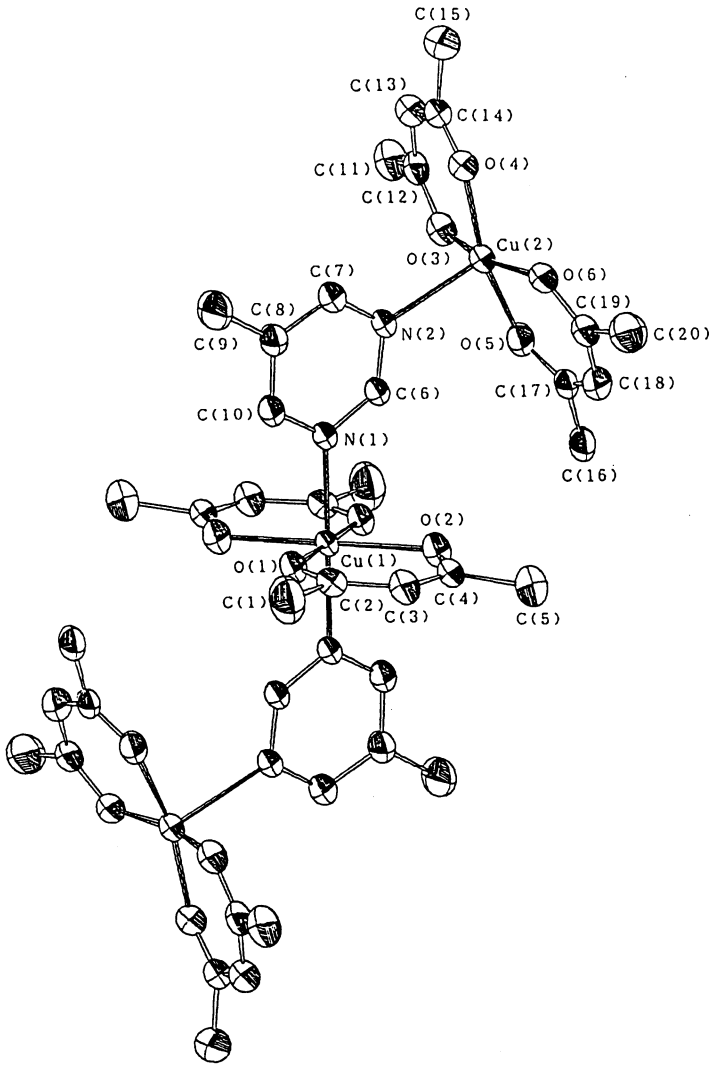
Reaction of $Cu(hfac)_2$ (Hhfac=1,1,1,5,5,5-hexafluoro-2,4-pentanedione) with 5-methylpyrimidine (5-pym) gave the title complex $[Cu(hfac)_2]_3(\mu\text{-}5\text{-}pym)_2$. The complex has been characterized by X-ray structure analysis and IR spectral measurements.

Recently, several X-ray investigations have been reported on the $Cu(hfac)_2$ with nitrogen ligands,[1-9] and a few of them are multinuclear complexes with bridging bidentate nitrogen ligands. For example, $Cu(hfac)_2(ted)$[4] (ted=1,4-diazabicyclo[2.2.2]octane), $Cu(hfac)_2(pyz)$ (pyz=pyrazine) and $[Cu(hfac)_2]_2(pyz)$[6] have been isolated and their structures determined by X-ray analyses. The copper atoms of these complexes situated in $Cu(hfac)_2$ are bridged with ted or pyz molecules. The bond lengths of Cu-N are 2.566(7) and 2.529(9) Å respectively in $Cu(hfac)_2(ted)$ and $Cu(hfac)_2(pyz)$, which have a geometry of tetragonal bipyramid around each copper atom, while the bond length of Cu-N is 2.250(17) Å in $[Cu(hfac)_2]_2(pyz)$,[6] which has a geometry of tetragonal pyramid around each copper atom.

As a part of continuing investigations on $Cu(hfac)_2$ complexes with nitrogen bases, we prepared a unique trinuclear complex composed of $Cu(hfac)_2$ with 5-pym molecules. Here we report X-ray crystal structure and IR spectral properties of the 5-methylpyrimidine complexes.

The complex $[Cu(hfac)_2]_3(\mu\text{-}5\text{-}pym)_2$ (**1**) was obtained as follows. $Cu(hfac)_2$ was dissolved in petroleum ether with an equimolar quantity of 5-methylpyrimidine. The solution was boiled under reflux for 1h. After



Bond lengths (l/Å)

Cu(1)···Cu(2)	5.976(1)
Cu(1)-O(1)	2.008(6)
Cu(1)-O(2)	2.192(6)
Cu(1)-N(1)	2.050(6)
Cu(2)-O(3)	1.960(6)
Cu(2)-O(4)	1.941(6)
Cu(2)-O(5)	1.934(6)
Cu(2)-O(6)	1.959(6)
Cu(2)-N(2)	2.282(5)

Bond angles (ϕ/°)

O(1)-Cu(1)-O(2)	88.7(2)
O(1)-Cu(1)-N(1)	90.3(2)
O(2)-Cu(1)-N(1)	88.9(2)
O(3)-Cu(2)-O(4)	92.1(2)
O(5)-Cu(2)-O(6)	91.8(2)

Fig. 1. Perspective view of **1**. Fluorine atoms of CF_3 groups are omitted for clarity.

standing for a few days, green crystals were formed. They were separated by filtration and dried in vacuo. $[Cu(hfac)_2]_3(\mu\text{-5-pym})_2$: Found: C, 29.50; H, 1.06; N, 3.57%. Calcd for $C_{40}H_{18}N_4O_{12}F_{36}Cu_3$: C, 29.64; H, 1.12; N, 3.46%. $[Cu(hfac)_2]_2(\mu\text{-5-pym})$ (**2**) and $Cu(hfac)_2(5\text{-pym})_2$ (**3**) were prepared by a similar method as described above. $[Cu(hfac)_2]_2(\mu\text{-5-pym})$: C, 28.46; H, 0.97; N, 2.91%. Calcd for $C_{25}H_{10}N_2O_8F_{24}Cu_2$: C, 28.61; H, 0.96; N, 2.67%. $Cu(hfac)_2(5\text{-pym})_2$: C, 35.98; H, 2.07; N, 8.68%. Calcd for $C_{20}H_{14}N_4O_4F_{12}Cu$: C, 36.08; H, 2.12; N, 8.41%. IR spectral data are given in Table 1.

X-Ray structure analysis[10] of **1** shows that two copper atoms are linked by 5-pym molecule with a separation of 5.976(1) Å (Fig. 1). The geometry about Cu(1) atom is approximately a tetragonal bipyramid. The

axial positions of Cu(1) atom are occupied by two oxygen atoms one from each of the bidentate hfac ligands. The other oxygen atoms from the hfac ligand are in the basal plane with two nitrogen atoms from 5-pym molecules. The axial oxygen atoms have a long Cu(1)-O(2) distance (2.192(6) Å), which is longer than that of equatorial Cu(1)-O(1) (2.008(6) Å) or Cu(1)-N(1) (2.050(6) Å) in this adduct. The coordination around Cu(1) atom is similar to that of $Cu(hfac)_2(4\text{-}Hmpz)_2$, however, the Cu(1)-O(2) distance is not so long as that of Cu-O(2) (2.346(6) Å) in $Cu(hfac)_2(4\text{-}Hmpz)_2$.[9] On the other hand, the geometry around Cu(2) atom is a tetragonal pyramid with the nitrogen atom N(2) from 5-pym molecule at the apex. Although the basicity of 5-pym molecule is essentially stronger than that of pyz molecule, Cu(2)-N(2) distance is similar to or slightly longer (2.282(5) Å) than that of $[Cu(hfac)_2]_2(pyz)$[6] (2.250(17) Å). This may result from a mutual repulsion between the hfac ligands coordinated to Cu(1) and Cu(2) atoms.

The complexes **2** and **3** are also obtained by the stoichiometric reactions of $Cu(hfac)_2$ with 5-pym molecule, and are five- and six-coordinated complexes, respectively. In **2**, the two copper atoms are linked by 5-pym molecule.

The IR spectrum of **1** has two bands in C-O stretching region at 1653.6 and 1642.0 cm^{-1} with approximate intensities of 1:2, respectively (Table 1). The former is assigned to the C-O stretching vibration of hfac ligands around six-coordinated copper atom Cu(1), and the latter to that of hfac ligands around five-coordinated copper atom Cu(2). The split bands are also observed at 680.3 and 672.0 cm^{-1} with approximate intensities of 2:1, respectively. These are assignable to the ring deformation of hfac rings around five- and six-coordinated copper atoms, respectively. No split band of CF_3 deformation ($\delta_s CF_3$) is observed at 596.8 cm^{-1}, and this may probably be an overlapped band. In **1**, the νC-O band of 1642.0 cm^{-1} is shifted to the lower frequency side from the band of 1646.4 cm^{-1} in **2**, while that of 1653.6 cm^{-1} is shifted to the higher frequency side from that of 1650.3 cm^{-1} in **3**. The shifts of νC-O bands probably arise from a mutual

Table 1. IR Spectral Data of the Complexes

Complex	Assignment/cm^{-1}		
	νC-O	ring def.	$\delta_s CF_3$
1 $[Cu(hfac)_2]_3(\mu\text{-}5\text{-}pym)_2$	1653.6	680.3	596.8
	1642.0	672.0	
2 $[Cu(hfac)_2]_2(\mu\text{-}5\text{-}pym)$	1646.4	680.2	597.2
3 $Cu(hfac)_2(5\text{-}pym)_2$	1650.3	670.1	588.1

repulsion between the hfac ligands around five- and six-coordinated copper atoms. This is in agreement with the result of X-ray analysis described above.

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References

1) M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, J. Am. Chem. Soc., **91**, 1859 (1969).
2) 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.
3) M. R. Truter and B. L. Vickery, J. Chem. Soc., Dalton Trans., **1972**, 395.
4) R. C. E. Belford, D. E. Fenton, and M. R. Truter, J. Chem. Soc., Dalton Trans., **1972**, 2208.
5) J. Pradilla-Sorzano and J. P. Fackler Jr., Inorg. Chem., **12**, 1174 (1973).
6) R. C. E. Belford, D. E. Fenton, and M. R. Truter, J. Chem. Soc., Dalton Trans., **1974**, 17.
7) N. A. Bailey, D. E. Fenton, M. V. Franklin, and M. Hall, J. Chem. Soc., Dalton Trans., **1980**, 984.
8) T. Kogane, M. Ishii, K. Harada, R. Hirota, and M. Nakahara, Bull. Chem. Soc. Jpn., **62**, 2524 (1989).
9) T. Kogane, M. Ishii, K. Harada, R. Hirota, and M. Nakahara, Bull. Chem. Soc. Jpn., **63**, 1005 (1990).
10) The crystal data are as follows: $C_{40}H_{18}N_4O_{12}F_{36}Cu_3$, MW=1621.18, triclinic, $P\bar{1}$, a=11.875(1), b=13.714(1), c=11.411(1) Å, α=91.28(1), β=116.51(1), γ=64.59(1)°, U=1468.9(4) Å^3, Z=1, and R=0.065. The X-ray diffraction data were collected by use of an automated four-circle diffractometer, Rigaku AFC-4, with a graphite-monochromated MoKα radiation (λ=0.71073 Å) up to 2θ=60°, the θ-2θ scan technique being employed. Independent reflections with $|F_o| > 3\sigma(|F_o|)$, 4363 reflections for **1**, was used for the structure determinations. The structure was solved by the heavy atom method (UNICS-III[11]), and refined by standard Patterson, Fourier, and block-diagonal least-squares techniques.
11) T. Sakurai and K. Kobayashi, Rikagaku Kenkyusho Hokoku, **55**, 69 (1978).

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