Preparation and Characterisation of Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II) Complexes with Diazaaromatic Compounds. Part 1. Crystal Structures and Characterisation of Several Adducts with Diazines†

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The reactions of $[Cu(hfac)_2]$ (Hhfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) with diazines (tmpyz = 2,3,5-trimethylpyrazine, mpym = 5-methylpyrimidine and mpydz = 3-methylpyridazine) in light petroleum have been studied and the following complexes obtained: $[\{Cu(hfac)_2\}_3(\mu\text{-}tmpyz)_2]$ **1b**, $[Cu(hfac)_2(tmpyz)]$ **1e**, $[\{Cu(hfac)_2(\mu\text{-}mpym)\}_n]$ **2a**, $[\{Cu(hfac)_2\}_3(\mu\text{-}mpym)_2]$ **2b**, $[\{Cu(hfac)_2\}_2(\mu\text{-}mpym)]$ **2c**, $[Cu(hfac)_2(mpym)_2]$ **2d**, and $[Cu(hfac)_2(mpydz)_2]$ **3d**. The crystal structures of **1b**, **2b** and **3d** have been determined. Although **1b** and **2b** are both trinuclear complexes with bridging diazole molecules, the geometry around atom Cu(2) is trigonal bipyramidal for **1b** and tetragonal pyramidal for **2b**. The geometry around atom Cu(1) is tetragonal bipyramidal in both complexes. The distance Cu(1)–N(1) is longer in **1b** than in **2b**, while the Cu(2)–N(2) is somewhat shorter in the former. The steric effects of the ligands on the structural differences between these complexes are discussed. On the basis of the relation between the geometry of the co-ordinated hfac ligands and ν(C–O) values, structures of some of the other complexes are suggested.

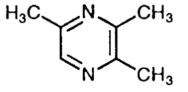
Several X-ray investigations have been reported on the reaction products of $[Cu(hfac)_2]$ with nitrogen bases,[1–10] nitroxyl radicals[11–14] and nitroxide.[15] Some of them are multinuclear complexes with bridging bidentate ligands. For example, two kinds of μ-pyrazine (pyz) complexes $[\{Cu(hfac)_2(\mu\text{-}pyz)\}_n]$ and $[\{Cu(hfac)_2\}_2(\mu\text{-}pyz)]$ have been reported.[6] The former is a linear co-ordination polymer with a tetragonal-bipyramidal geometry around each copper atom, while the latter is a dinuclear complex and each copper atom has a tetragonal-pyramidal geometry. Several trinuclear complexes have also been reported.[16]

So far we have investigated the reaction of $[Cu(hfac)_2]$ with pyrazoles,[8,9,17] and are now interested in the reaction with diazines. Here we report the crystal structures of some of the complexes synthesised by the reaction of $[Cu(hfac)_2]$ with the diazines 2,3,5-trimethylpyrazine (tmpyz), 5-methylpyrimidine (mpym) and 3-methylpyridazine (mpydz). Characterisation by IR spectroscopy is also included. We have already briefly published the structure of one of the reaction products $[\{Cu(hfac)_2\}_3(\mu\text{-}mpym)_2]$ elsewhere.[10]

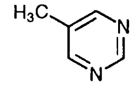
Results and Discussion

Preparation.—The products of reaction of $[Cu(hfac)_2]$ with the diazines are shown in Scheme 1. Here, the notation **a**, **b**, **c** and **d** (or **e**) denotes polymeric, tri-, di- and mono-nuclear respectively.

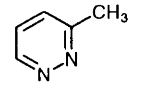
Crystal Structures.—Perspective views of complexes **1b**, **2b** and **3d** are shown in Figs. 1, 2 and 3 with the atomic numbering. Crystallographic data are listed in Table 1, final atomic coordinates in Tables 2–4, and the geometries of the metal co-ordination sphere, in Tables 5–7.



tmpyz



mpym



mpydz

Complex **1b**. The complex is trinuclear and two adjacent copper atoms 7.280(3) Å apart are linked by a tmpyz molecule. The geometry about atom Cu(2) is approximately trigonal bipyramidal with the nitrogen atom N(2) from tmpyz at the equatorial position. The axial Cu(2)–O(3) and Cu(2)–O(5) distances are somewhat shorter than the equatorial Cu(2)–O(4), Cu(2)–O(6) and Cu(2)–N(2) distances (Table 5). Thus the co-ordination geometry around atom Cu(2) is of a compressed N-equatorial trigonal-bipyramidal type. A trigonal-bipyramidal geometry in similar adducts has been reported only for $[\{Cu(hfac)_2\}_3(\mu\text{-}L)_2]$[12] (L = 2,2,5,5-tetramethyl-4-phenyl-3-imidazolin-1-yloxyl), in which the geometry around two copper atoms is distorted N-equatorial bipyramidal.

In tmpyz the environment around nitrogen atom N(2) is more crowded than that of N(1) and the neighbouring methyl groups hinder access of N(2) to the chelated Cu(2). The N(2)–Cu(2)–O(4) and N(2)–Cu(2)–O(6) bond angles are 135.0(4) and 135.6(4)° respectively. These large angles arise from substantial steric interaction from the methyl groups. The resultant bond angle of O(4)–Cu(2)–O(6) is only 89.4(4)°. This value is unusually low and the nearest trigonal angle to this

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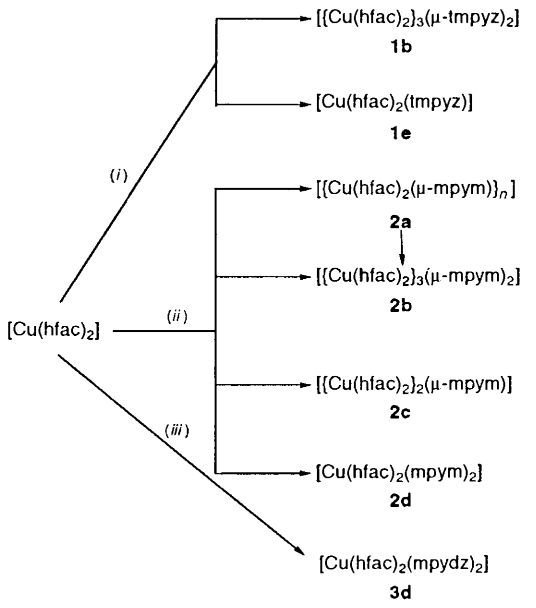
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 Products of reaction of $[Cu(hfac)_2]$ with diazines. (*i*) tmpyz; (*ii*) mpym; (*iii*) mpydz

value ever reported is 91.4(3)° in $[Cu(py)_3(O_2NO)_2]$ (py = pyridine).[18] Comparably small trigonal angles have been observed for some other trinuclear copper complexes.[13,14] It is suggested that the geometry about Cu(2) in **1b** may stabilise the complex by decreasing the repulsion between the hfac ligands and the methyl group.

The geometry about copper atom Cu(1) is approximately tetragonal bipyramidal. The axial positions are occupied by 1-nitrogen atoms of the two tmpyz molecules, and the four equatorial positions are occupied by oxygen atoms from the bidentate hfac ligands. The Cu(1)–N(1)–C(6) bond angle [133.2(8)°] is larger than that of Cu(1)–N(1)–C(12) [107.7(8)°], while Cu(2)–N(2)–C(8) and Cu(2)–N(2)–C(10) [122.7(8) and 119.1(8)° respectively] are normal. Furthermore, the distance from the nitrogen atom N(1) to the plane formed by the atoms Cu(1), C(6) and C(12) is 0.668(14) Å, while N(2) is in the plane formed by Cu(2), C(8) and C(10). Thus, the 2-methyl group also hinders approach of the Cu(1) atom to N(1).

Complex **2b**. Although **2b** is also a trinuclear complex its structure is rather different from that of **1b**. In **2b** two adjacent copper atoms 5.976(1) Å apart are linked by a mpym molecule. The geometry about atom Cu(1) is approximately tetragonal bipyramidal. The axial positions are occupied by two oxygen atoms, one from each bidentate hfac ligand. The other oxygen atoms from the hfac ligands are in the basal plane with two nitrogen atoms of mpym molecules. The axial oxygen atoms have a long Cu(1)–O(2) distance (Table 6). Thus, the co-ordination geometry of Cu(1) is classified as *trans*-N_2O_2 octahedral and is similar to that of $[Cu(hfac)_2(4\text{-}Hmpz)_2]$ (4-Hmpz = 4-methyl-1*H*-pyrazole).[9] On the other hand, the geometry around atom Cu(2) is tetragonal pyramidal with atom N(2) from mpym at the apex. Although the basicity of mpym is essentially higher than that of pyz, the Cu(2)–N(2) distance is similar to, or slightly longer than, that of $[\{Cu(hfac)_2\}_2(\mu\text{-}pyz)]$[6] [2.250(17) Å]. This may result from a mutual repulsion between the hfac ligands co-ordinated to Cu(1) and Cu(2). Atom Cu(2) lies 0.228(3) Å above the basal plane.

As described, the co-ordination geometries of complexes **1b** and **2b** around Cu(1) as well as Cu(2) are quite different, probably due to the steric differences around the co-ordinating nitrogen atoms between the diazine ligands.

Complex **3d**. The molecule has a centre of symmetry and the geometry about each copper atom is approximately tetragonal bipyramidal. The co-ordination geometry of Cu belongs to the *trans*-N_2O_2 octahedral type, being similar to that of Cu(1) in complex **2b**. The two mpydz molecules are co-ordinated by the less hindered 1-nitrogen atoms. Compared with the structure of **2b**, the Cu–O(1) and Cu(1)–N(1) distances are similar, while Cu–O(2) is somewhat longer. The C(2)–O(1) and C(4)–O(2) distances are different (Table 8). Different C–O distances have also been observed in $[Zn(hfac)_2(py)_2]$[5] and in chelate ring 2 of $[Cu(hfac)_2(5\text{-}Hmpz)]$ (5-Hmpz = 5-methyl-1*H*-pyrazole).[8]

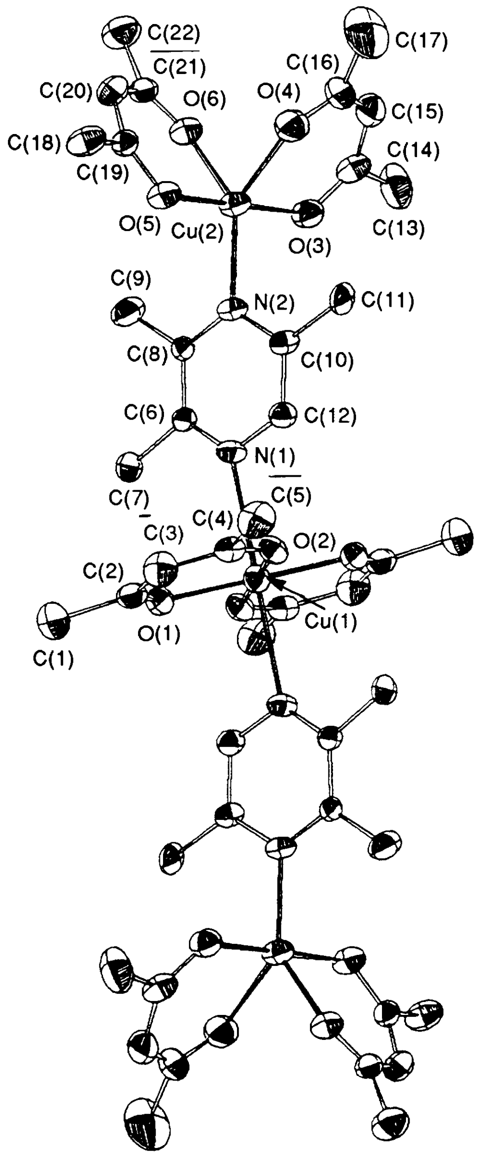


Fig. 1 A perspective drawing of the structure of complex **1b**, showing the atom numbering scheme (30% probability thermal ellipsoids). Unlabelled atoms are related to labelled ones by the inversion centre. Fluorine atoms attached to C(1), C(5), C(13), C(17), C(18) and C(22) are omitted for clarity

Infrared Study.—The IR spectrum of complex **1b** has three bands in C–O stretching region at 1658, 1644 and 1639 cm^{-1} with approximate intensities of 1 : 1 : 1, respectively. On the basis of many IR spectral data concerning a series of the adducts of $[Cu(hfac)_2]$ with bases,[4–6,8–10] the ν(C–O) band at 1644 cm^{-1} is assigned to the C–O stretching vibration of the hfac ligands around the six-co-ordinated copper atom Cu(1), and the other two bands may correspond to the non-equivalent C–O bonds. Similarly split ν(C–O) bands were observed for $[Zn(hfac)_2(py)_2]$[5] and in the hfac chelate ring 2 of $[Cu(hfac)_2(5\text{-}Hmpz)]$.[8]

The IR spectrum of complex **1e** has a single band in the C–O stretching region at 1639 cm^{-1}. This relatively low value

Table 1 Crystallographic data and experimental details for complexes **1b**, **2b** and **3d**[a]

	1b	**2b**	**3d**
Molecular formula	$C_{44}H_{26}Cu_3F_{36}N_4O_{12}$	$C_{40}H_{18}Cu_3F_{36}N_4O_{12}$	$C_{20}H_{14}CuF_{12}N_4O_4$
M	1677.29	1621.18	665.88
Crystal system	Triclinic	Triclinic	Monoclinic
Crystal colour	Green	Green	Green
Crystal size/mm	0.33 × 0.27 × 0.05	0.4 × 0.35 × 0.45	0.4 × 0.2 × 0.45
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$
a/Å	9.070(2)	11.875(1)	10.797(3)
b/Å	19.367(3)	13.714(1)	14.583(2)
c/Å	8.956(2)	11.411(1)	7.973(1)
α/°	97.30(1)	91.28(1)	90
β/°	98.20(2)	116.51(1)	97.70(2)
γ/°	84.04(1)	64.59(1)	90
U/Å^3	1538.6(4)	1468.9(4)	1243.8(4)
Z	1	1	2
D_c/Mg m^{-3}	1.81	1.83	1.778
F(000)	825	793	662
μ(Mo-Kα)/cm^{-1}	11.9	12.5	10.0
No. of reflections measured	6717	6379	3661
No. of unique data used	3023 ($\|F_o\| > 2.5\sigma\|F_o\|$)	4363 ($\|F_o\| > 3\sigma\|F_o\|$)	2527 ($\|F_o\| > 2.5\sigma\|F_o\|$)
R^b	0.100	0.065	0.070

[a] Details in common: scan rate 4° min^{-1}; scan range $2\theta \leqslant 60°$. [b] $R = \Sigma|F_o| - |F_o|/\Sigma|F_o|$ (unit weights).

Table 2 Atomic coordinates (× 10^4) for [{Cu(hfac)$_2$}$_3$(μ-tmpyz)$_2$] **1b** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Cu(1)	5 000	5 000	5 000	O(6)	3 497(11)	963(5)	9 129(10)
Cu(2)	2 752(2)	1 984(1)	9 770(2)	N(1)	4 622(12)	3 893(5)	13 197(12)
F(1)	9 350(12)	4 928(6)	2 838(15)	N(2)	3 572(12)	2 786(5)	11 231(10)
F(2)	9 281(13)	5 880(7)	4 144(17)	C(1)	8 611(19)	5 528(10)	2 966(21)
F(3)	8 709(14)	5 843(10)	1 807(19)	C(2)	6 960(16)	5 465(7)	3 212(15)
F(4)	2 225(14)	6 484(8)	1 855(16)	C(3)	5 815(18)	5 746(9)	2 206(17)
F(5)	2 289(16)	5 577(8)	545(16)	C(4)	4 327(15)	5 733(6)	2 390(14)
F(6)	3 591(14)	6 316(12)	260(19)	C(5)	3 155(20)	6 028(9)	1 242(18)
F(7)	−463(20)	703(12)	12 614(19)	C(6)	5 508(13)	3 328(6)	12 853(14)
F(8)	−81(24)	1 650(11)	13 573(19)	C(7)	7 119(15)	3 364(7)	13 567(18)
F(9)	1 615(13)	903(9)	13 562(15)	C(8)	5 008(13)	2 779(7)	11 848(13)
F(10)	−970(21)	945(11)	6 285(15)	C(9)	6 022(18)	2 145(8)	11 422(17)
F(11)	−2 440(17)	1 009(14)	7 612(18)	C(10)	2 626(14)	3 355(6)	11 622(14)
F(12)	−1 921(22)	1 836(9)	6 706(27)	C(11)	997(15)	3 347(8)	10 993(17)
F(13)	2 892(14)	2 713(6)	5 233(13)	C(12)	3 182(14)	3 913(7)	12 624(14)
F(14)	5 160(13)	2 735(6)	6 108(12)	C(13)	539(19)	1 111(13)	12 751(20)
F(15)	4 456(15)	1 898(6)	4 449(11)	C(14)	793(18)	1 358(7)	11 263(16)
F(16)	3 614(15)	−376(5)	8 375(14)	C(15)	−241(18)	1 233(9)	9 980(18)
F(17)	5 502(15)	−211(6)	7 490(24)	C(16)	−194(16)	1 480(9)	8 650(19)
F(18)	3 479(19)	−252(6)	6 119(14)	C(17)	−1 407(25)	1 351(17)	7 426(25)
O(1)	6 864(10)	5 147(5)	4 307(10)	C(18)	4 066(20)	2 311(8)	5 648(16)
O(2)	3 837(9)	5 478(4)	3 390(10)	C(19)	3 829(14)	1 897(7)	6 943(14)
O(3)	1 922(11)	1 694(5)	11 408(10)	C(20)	3 955(17)	1 182(8)	6 691(14)
O(4)	763(12)	1 840(6)	8 365(12)	C(21)	3 811(15)	773(7)	7 834(15)
O(5)	3 541(11)	2 302(5)	8 113(10)	C(22)	4 102(21)	−17(9)	7 462(20)

indicates an N-axial square-pyramidal structure with a tmpyz molecule at the apex.[6,10]

The spectrum of complex **2b** has two bands in the C–O stretching region at 1654 and 1642 cm^{-1}, which are assigned to the vibrations of the hfac ligands around the six-co-ordinated copper atom Cu(1) and around the five-co-ordinated atom Cu(2) respectively.[10] On the other hand, the spectrum of **2a** has a broad band at 1651 cm^{-1} with a shoulder at about 1670 cm^{-1}. The ν(C–O) value of **2a** is similar to that of **2d** (1650 cm^{-1}), though the shoulder is at a rather higher wavenumber. Thus, **2a** may be a co-ordination polymer consisting of six-co-ordinated copper atoms. Actually, **2a** yielded **2b** on standing for a few months or longer in the atmosphere.

For complex **3d**, split ν(C–O) bands were also observed at 1672 and 1656 cm^{-1}. The splitting may arise from non-equivalent C–O bonds in each hfac chelate ring as described above.

Experimental

Materials.—Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-copper(II) was prepared by the reported method.[19] 2,3,5-Trimethylpyrazine, 3-methylpyridazine (Aldrich Chemical Co.), and 5-methylpyrimidine (Sigma Chemical Co.) were used without further purification.

Preparations.—[{Cu(hfac)$_2$}$_3$(μ-tmpyz)$_2$] **1b** *and* [Cu(hfac)$_2$-(tmpyz)] **1e**. The complex [Cu(hfac)$_2$] was dissolved in light petroleum (b.p. range 30–70 °C) with an equimolar quantity of 2,3,5-trimethylpyrazine. The solution was boiled under reflux for 1 h. After standing for a few days, light green (the major product) and green crystals (the minor product) were formed. The green crystals were carefully separated from the light green crystals, washed and dried *in vacuo*. The light green crystals were obtained by a similar method.

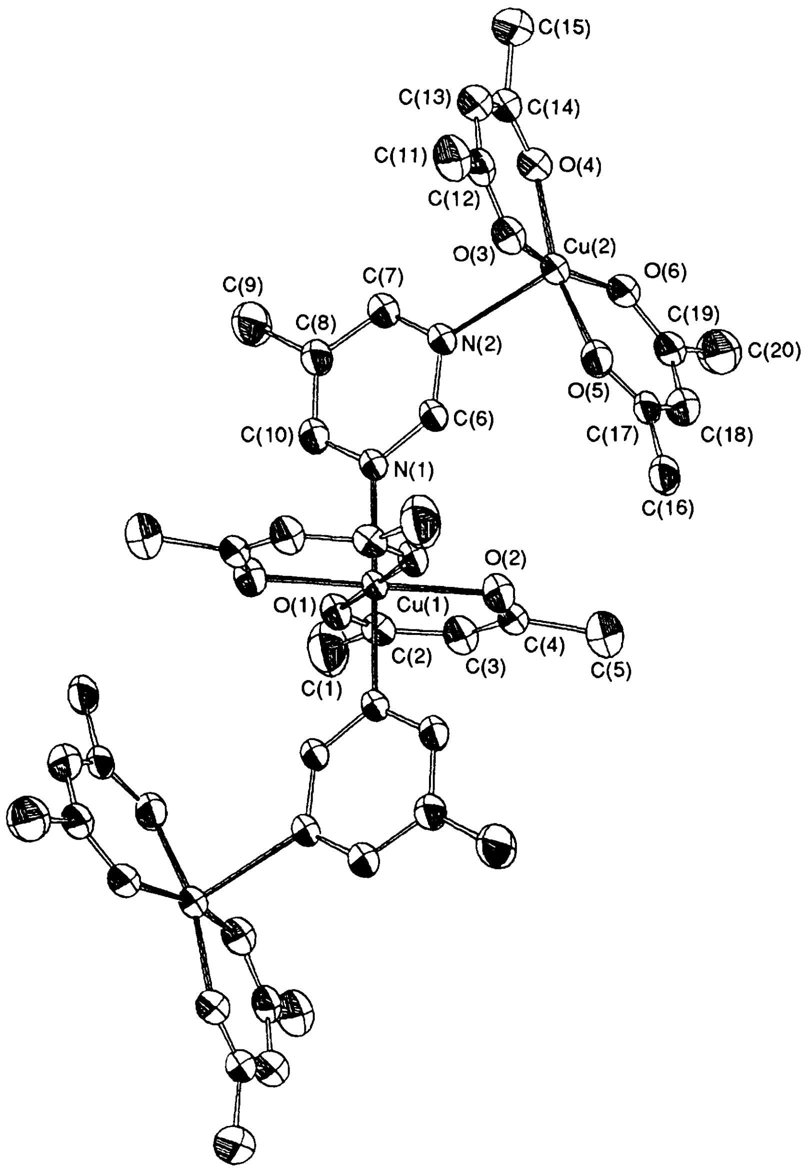


Fig. 2 A perspective drawing of the structure of complex **2b**, showing the atom numbering scheme (30% probability thermal ellipsoids). Unlabelled atoms are related to labelled ones by the inversion centre. Fluorine atoms attached to C(1), C(5), C(11), C(15), C(16) and C(20) are omitted for clarity

[{Cu(hfac)$_2$}$_3$(μ-mpym)$_2$] **2b** *and* [{Cu(hfac)$_2$(μ-mpym)}$_n$] **2a**. The complex [Cu(hfac)$_2$] was dissolved in light petroleum with an equimolar quantity of 5-methylpyrimidine. The solution was boiled under reflux for 1 h. After standing for a few days, light green needles were formed. They were recrystallised from light petroleum. After standing for several days, light green needles (the major product) and green crystals (the minor product) were formed. The green crystals were carefully separated from the light green needles, washed and dried *in vacuo*. The light green needles were obtained by a similar method.

[{Cu(hfac)$_2$}$_2$(μ-mpym)] **2c** *and* [Cu(hfac)$_2$(mpym)$_2$] **2d**. The complex [Cu(hfac)$_2$] was dissolved in light petroleum with stoichiometric quantities of 5-methylpyrimidine. The solution was boiled under reflux for 1 h. After standing for a few days, light green or green crystals were formed. They were filtered off and dried *in vacuo*.

[Cu(hfac)$_2$(mpydz)$_2$] **3d**. This complex was prepared by a similar method to that described above.

Microanalytical data for the new complexes are given in Table 9.

Spectral Measurements.—The IR spectra were recorded on a Nicolet 5ZDX Fourier-transform spectrophotometer.

Crystal Structure Analyses of Complexes **1b**, **2b** *and* **3d**.—The X-ray diffraction data were collected by use of an automated four-circle diffractometer, Rigaku AFC-4, with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) up to 2θ = 60°, with the θ–2θ scan technique. Five standard reflections were monitored every 50. No decomposition of the crystals was observed. The usual corrections for Lorentz and polarisation effects were made but no absorption correction was applied.

For the structure determinations, 3023, 4363 and 2527 independent reflections for complexes **1b**, **2b** and **3d** respectively, were used. Calculations were carried out on a ACOS 2000 computer at the Tohoku University Computer Centre using the UNICS III[20] and ORTEP programs.[21] The atomic scattering factors including the anomalous scattering factors were taken from ref. 22 for non-hydrogen atoms and from ref. 23 for hydrogen. 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

Table 3 Atomic coordinates (× 10^4) for [{Cu(hfac)$_2$}$_3$(μ-mpym)$_2$] **2b** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0	10 000	0
Cu(2)	4 055(1)	5 182(1)	2 115(1)
F(1)	−839(9)	9 102(8)	3 265(6)
F(2)	−2 374(9)	8 659(10)	2 110(7)
F(3)	−201(11)	7 659(7)	2 718(10)
F(4)	−4 709(11)	9 513(9)	−2 567(9)
F(5)	−5 025(13)	11 076(9)	−3 085(15)
F(6)	−3 803(19)	9 837(17)	−3 624(13)
F(7)	1 799(7)	3 339(7)	2 929(6)
F(8)	797(7)	3 292(7)	941(8)
F(9)	215(6)	4 779(6)	1 534(9)
F(10)	6 449(6)	1 710(5)	1 597(7)
F(11)	5 435(7)	2 668(5)	−350(6)
F(12)	4 631(7)	1 668(5)	61(7)
F(13)	4 601(6)	7 659(5)	5 673(6)
F(14)	2 541(6)	8 120(4)	4 074(5)
F(15)	3 621(7)	6 689(5)	5 607(6)
F(16)	7 695(8)	6 726(6)	3 833(9)
F(17)	8 646(6)	5 047(7)	4 561(8)
F(18)	−2 219(8)	5 633(7)	2 500(8)
F(X1)	−5 278(20)	10 459(31)	−2 446(26)
F(X2)	−3 934(22)	9 173(13)	−3 046(19)
F(X3)	−4 599(21)	10 750(14)	−3 653(14)
O(1)	−321(5)	9 343(4)	1 304(5)
O(2)	−2 121(5)	10 324(4)	−1 574(5)
O(3)	2 645(5)	4 781(4)	2 082(5)
O(4)	4 717(5)	3 993(4)	1 250(5)
O(5)	3 680(5)	6 092(4)	3 348(5)
O(6)	5 761(5)	5 326(4)	2 541(5)
N(1)	832(5)	8 489(4)	−461(5)
N(2)	2 456(5)	6 603(4)	292(5)
C(1)	−1 208(12)	8 641(9)	2 269(10)
C(2)	−1 365(8)	9 200(6)	1 038(7)
C(3)	−2 558(8)	9 445(6)	−175(8)
C(4)	−2 815(7)	9 953(5)	−1 376(7)
C(5)	−4 166(11)	10 098(8)	−2 669(10)
C(6)	1 746(7)	7 585(5)	479(6)
C(7)	2 209(7)	6 522(8)	−979(7)
C(8)	1 224(8)	7 431(6)	−2 039(7)
C(9)	947(12)	7 337(8)	−3 463(9)
C(10)	550(7)	8 426(6)	−1 739(7)
C(11)	1 319(9)	3 861(8)	1 779(9)
C(12)	2 463(7)	3 994(6)	1 606(7)
C(13)	3 164(8)	3 259(6)	1 042(8)
C(14)	4 270(7)	3 286(5)	968(7)
C(15)	5 190(9)	2 317(7)	554(9)
C(16)	3 771(9)	7 281(7)	4 843(7)
C(17)	4 392(7)	6 571(5)	4 018(6)
C(18)	5 561(8)	6 530(7)	4 035(8)
C(19)	6 171(7)	5 908(6)	3 330(8)
C(20)	7 572(9)	5 866(8)	3 504(11)

Table 4 Atomic coordinates (× 10^4) for [Cu(hfac)$_2$(mpydz)$_2$] **3d** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu	5 000	5 000	5 000
F(1)	1 546(4)	5 851(3)	1 169(8)
F(2)	1 482(4)	4 620(5)	−236(6)
F(3)	1 068(4)	4 639(4)	2 236(8)
F(4)	4 784(6)	2 390(4)	570(11)
F(5)	6 476(6)	2 690(5)	1 583(9)
F(6)	5 718(10)	3 255(4)	−650(9)
N(1)	3 989(4)	3 893(3)	5 608(5)
N(2)	4 303(4)	3 077(3)	5 027(6)
O(1)	3 556(3)	5 296(2)	3 221(4)
O(2)	5 774(3)	4 201(2)	2 910(5)
C(1)	1 823(5)	4 991(5)	1 212(8)
C(2)	3 194(5)	4 802(3)	1 954(6)
C(3)	3 796(5)	4 117(4)	1 208(7)
C(4)	5 038(5)	3 869(3)	1 755(6)
C(5)	5 549(6)	3 071(4)	805(8)
C(6)	3 577(5)	2 355(3)	5 218(7)
C(7)	3 949(7)	1 471(4)	4 477(10)
C(8)	2 510(5)	2 420(4)	6 004(8)
C(9)	2 217(5)	3 251(4)	6 629(8)
C(10)	2 990(5)	3 988(4)	6 387(7)

Table 5 Selected bond lengths (Å) and angles (°) for complex **1b**

Cu(1) · · · Cu(2)	7.280(3)		
Cu(1)–O(1)	1.941(9)	Cu(1)–O(2)	1.937(8)
Cu(1)–N(1)	2.537(10)	Cu(2)–O(3)	1.910(11)
Cu(2)–O(4)	2.069(10)	Cu(2)–O(5)	1.929(10)
Cu(2)–O(6)	2.060(9)	Cu(2)–N(2)	2.030(9)
O(1)–Cu(1)–O(2)	91.3(4)	O(1)–Cu(1)–N(1)	93.8(4)
O(2)–Cu(1)–N(1)	85.4(3)	O(3)–Cu(2)–O(4)	90.0(4)
O(3)–Cu(2)–O(5)	178.2(4)	O(3)–Cu(2)–O(6)	90.0(4)
O(4)–Cu(2)–O(5)	89.1(4)	O(4)–Cu(2)–O(6)	89.4(4)
O(5)–Cu(2)–O(6)	91.6(4)	O(3)–Cu(2)–N(2)	88.4(4)
O(4)–Cu(2)–N(2)	135.0(4)	O(5)–Cu(2)–N(2)	91.1(4)
O(6)–Cu(2)–N(2)	135.6(4)		

Table 6 Selected bond lengths (Å) and angles (°) for complex **2b**

Cu(1) · · · Cu(2)	5.976(1)		
Cu(1)–O(1)	2.008(7)	Cu(1)–O(2)	2.192(5)
Cu(1)–N(1)	2.050(5)	Cu(2)–O(3)	1.960(7)
Cu(2)–O(4)	1.941(5)	Cu(2)–O(5)	1.934(6)
Cu(2)–O(6)	1.959(6)	Cu(2)–N(2)	2.282(5)
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(3)–Cu(2)–O(5)	85.8(3)	O(3)–Cu(2)–O(6)	166.6(2)
O(4)–Cu(2)–O(5)	166.6(2)	O(4)–Cu(2)–O(6)	87.2(2)
O(5)–Cu(2)–O(6)	91.8(2)	O(3)–Cu(2)–N(2)	94.8(2)
O(4)–Cu(2)–N(2)	100.0(2)	O(5)–Cu(2)–N(2)	93.4(2)
O(6)–Cu(2)–N(2)	95.5(2)		

Table 7 Selected bond lengths (Å) and angles (°) for complex **3d**

Cu–O(1)	2.009(3)	Cu–O(2)	2.228(4)
Cu–N(1)	2.043(4)		
O(1)–Cu–O(2)	85.4(1)	O(1)–Cu–N(1)	87.1(1)
O(2)–Cu–N(1)	91.7(2)	Cu–O(1)–C(2)	124.9(3)
Cu–O(2)–C(4)	118.9(3)		

Table 8 C–O bond lengths (Å) for complexes **1b**, **2b** and **3d**

Five-co-ordinated				
1b	C(14)–O(3)	C(16)–O(4)	C(19)–O(5)	C(21)–O(6)
	1.252(19)	1.242(21)	1.268(15)	1.235(16)
2b	C(12)–O(3)	C(14)–O(4)	C(17)–O(5)	C(19)–O(6)
	1.255(10)	1.266(11)	1.268(10)	1.263(10)
Six-co-ordinated				
		1b	**2b**	**3d**
	C(2)–O(1)	1.240(18)	1.239(12)	1.260(6)
	C(4)–O(2)	1.231(17)	1.234(13)	1.232(6)

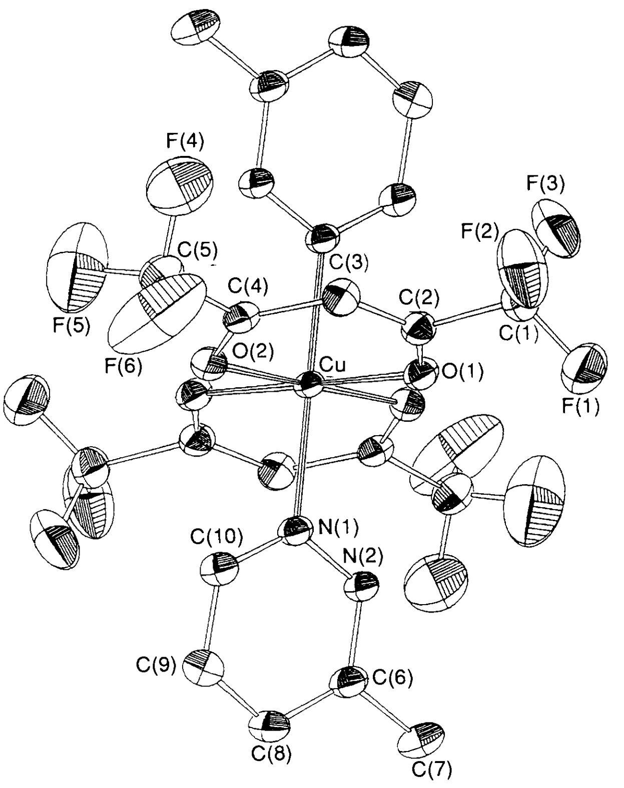


Fig. 3 A perspective drawing of the structure of complex **3d**, showing the atom numbering scheme (30% probability thermal ellipsoids). Unlabelled atoms are related to labelled ones by the inversion centre

Table 9 Microanalytical data for the complexes of [Cu(hfac)$_2$] with diazine

	Analysis (%)*		
Complex	C	H	N
1b	31.6 (31.5)	1.7 (1.6)	3.2 (3.3)
1e	34.0 (34.0)	2.4 (2.0)	4.7 (4.7)
2a	31.5 (31.5)	1.4 (1.4)	5.1 (4.9)
2b	29.5 (29.6)	1.1 (1.1)	3.6 (3.5)
2c	28.5 (28.6)	1.0 (1.0)	2.9 (2.7)
2d	36.0 (36.1)	2.1 (2.1)	8.7 (8.4)
3d	36.1 (36.1)	2.6 (2.4)	8.6 (8.4)

* Required values are given in parentheses.

rotationally disordered about the C–C bonds. The greater uncertainty is reflected in the higher standard deviations for F(3), F(6), F(7), F(8), F(10), F(11) and F(12) in **1b**, F(2), F(3), F(5) and F(6) in **2b** and F(5) and F(6) in **3d**. In **2b**, F(4), F(5) and F(6) are disordered with the corresponding F(X1), F(X2) and F(X3). The populations of F(4), F(5), F(6), F(X1), F(X2) and F(X3) are multiplied by 0.64, 0.67, 0.64, 0.36, 0.33 and 0.36 respectively. The final *R* values were 0.100 for **1b**, 0.065 for **2b** and 0.070 for **3d** respectively.

Additional material available from the Cambridge Crystallographic Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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