Ternary Complexes of Copper(II) with Mixed Acetylacetonate and Nitrogen-containing Ligands

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Ternary complexes of the type Cu(β-diketonate)′(β-diketonate)″(L) have been prepared where L = *o*-phenanthroline (phen), 2,2′-bipyridyl (bipy), and *NNN′N′*-tetramethylethane-1,2-diamine (tmen), and the β-diketonates present are selected from acetylacetone (Hacac), trifluoroacetylacetone (Htfac), and hexafluoroacetylacetone (Hhfac). Three dimensional *X*-ray crystal-structure analyses (heavy atom method) of the complexes Cu(acac)(hfac)(phen), (1), and Cu(acac)(hfac)(phen)·$2H_2O$, (2), have been carried out. Both have $Z = 2$ in a triclinic unit cell with space group $P\bar{1}$ (C_i, no. 2). Complex (1) has dimensions $a = 12.623$, $b = 11.470$, $c = 8.111$ Å, $\alpha = 81.17$, $\beta = 92.484$, and $\gamma = 97.691°$, $R = 0.064\,6$, for 2 470 reflections; (2) has $a = 12.284$, $b = 14.437$, $c = 8.020$ Å, $\alpha = 78.417$, $\beta = 109.315$, and $\gamma = 113.073°$, $R = 0.054\,6$ for 3 583 reflections. The two molecules contain a five-co-ordinated copper atom attached to a bidentate phen molecule and a chelating acac anion. In (1) the fifth site is occupied by a unidentate hfac anion whereas in (2) it is filled by a water molecule. The non-co-ordinated hfac in (2) is hydrogen bonded both to this water molecule and to a further unco-ordinated water molecule.

THERE has been controversy in the recent literature concerning the existence of mixed acetylacetonatocopper(II) complexes.[1-3] As part of a continuing investigation into the achievement of co-ordinative saturation by copper(II) through use of substituted acetylacetonates,[4-8] we have prepared certain mixed-ligand species and observed their reaction with chelating nitrogen donors.

The complexes (acetylacetonato)copper(II) trifluoroacetonate, [Cu(acac)(tfac)], (acetylacetonato)copper(II) hexafluoroacetylacetonate, [Cu(acac)(hfac)], and (trifluoroacetylacetonato)copper(II) hexafluoroacetylacetonate, [Cu(tfac)(hfac)], were prepared by the method of Farona *et al.*,[1] and treated in stoicheiometric amount with *o*-phenanthroline (phen), 2,2′-bipyridyl (bipy), or *NNN′N′*-tetramethylethane-1,2-diamine (tmen) in dichloromethane or toluene.

TABLE 1

Chemical analyses of complexes

Complex	Analysis (%) [a] C	H	N
Cu(acac)(hfac)(tmen)	39.1	4.6	5.4
	(39.5)	(4.4)	(5.8)
Cu(acac)(hfac)(bipy)	46.1	3.4	5.3
	(45.7)	(3.1)	(5.3)
Cu(acac)(hfac)(phen)	48.8	3.2	4.9
	(48.0)	(2.9)	(5.1)
Cu(acac)(hfac)(phen)·$2H_2O$	45.7	3.5	4.6
	(45.1)	(3.4)	(4.8)
Cu(tfac)(hfac)(tmen)	35.7	4.2	5.1
	(35.6)	(3.9)	(5.2)
Cu(tfac)(hfac)(bipy) [b]	41.6	2.6	5.0
	(41.4)	(1.9)	(4.8)
Cu(tfac)(hfac)(bipy) [c]	41.7	2.9	5.6
	(41.4)	(1.9)	(4.8)
Cu(tfac)(hfac)(phen)·H_2O	42.8	2.5	4.2
	(42.5)	(2.4)	(4.5)

[a] Calculated values are given in parentheses. [b] Pale green. [c] Dark green.

The reaction of Cu(acac)(tfac) with the nitrogenous chelates (L) led only to the recovery of $Cu(acac)_2$ and $Cu(tfac)_2L$. The complexes $Cu(tfac)_2$(phen), $Cu(tfac)_2$(bipy), and $Cu(tfac)_2$(tmen) were characterised fully and have also been synthesised from their components.[9] The complexes Cu(acac)(hfac) and Cu(tfac)(hfac) gave compounds, the analyses of which indicated the isolation of ternary complexes (see Table 1).

X-Ray crystal-structure analyses have been carried out on the compounds Cu(acac)(hfac)(phen), (1), and Cu(acac)(hfac)(phen)·2 H_2O, (2).

RESULTS AND DISCUSSION

The ability of bis(β-diketonato)copper(II) complexes to behave as Lewis acids and to react with donor ligands to form addition compounds is well known.[10] The Lewis acidity of the β-diketonates is affected by the relative electron-withdrawing power of the substituents present.[11] Thus when the highly electronegative CF_3 group is introduced in place of the CH_3 group in acetylacetone the Lewis acidity is enhanced and ultimately, *e.g.* for bis(hexafluoroacetylacetonato)copper(II),[4] co-ordinative saturation of copper(II) may be achieved through addition of ligands. This enhancement is readily shown in the mixed β-diketonates of copper(II) where it is observed that Cu(hfac)(tfac) and Cu(acac)(hfac) readily form complexes with phen, bipy, and tmen, whereas Cu(acac)(tfac) gave only the corresponding complexes of $Cu(tfac)_2$.

The mass spectra of the parent mixed β-diketonates, CuA(B) (A and B are β-diketonates), and of the complexes, CuA(B)L (L = nitrogeneous chelate), were run. The compound CuA(B) gave the molecular ion, and CuA_2 and CuB_2. The latter peaks may arise from redistribution reactions within the spectrometer source, or from residual impurities of the parents if the mixed complexes are indeed mixtures of mostly CuA(B), with slight, but equal, amounts of CuA_2 and CuB_2 present (see

$$2\ CuA(B) \rightleftharpoons CuA_2 + CuB_2$$

equation).[2] All three mixed β-diketonates showed fragmentation patterns derived from these components, but interpretation of the patterns is not entirely unambiguous [*e.g.* the peak at 339 in the mass spectrum of Cu(acac)(hfac) may arise from Cu(acac)(hfac) − 2 CH_3 or from $Cu(hfac)_2$ − 2 CF_3]. The ternary complexes also showed peaks ascribable to the CuA_2 and CuB_2 species. However different fragmentation patterns were observed for CuA(B)(phen) compared with CuA(B)(bipy) and CuA(B)(tmen). The latter complexes decomposed readily to give CuA(B) and the ligand as the mass spectrum corresponded to a superposition of those for the components. For CuA(B)(phen) no decomposition was apparent and the spectra showed peaks corresponding to $Cu(hfac)(phen)^+$ and $Cu(phen)^+$, as well as the fragmenttion of CuA(B), CuA_2, and CuB_2. The mass spectra of $Cu(hfac)_2(phen)$ and $Cu(hfac)_2(bipy)$ have been shown to follow similar pathways.[12] The $Cu(hfac)_2(bipy)$ decomposes prior to fragmentation and peaks corresponding to $Cu(hfac)(phen)^+$ and $Cu(phen)^+$ are observed for $Cu(hfac)_2(phen)$. The increased rigidity of, and the increased d_π–p_π interaction in, the phen adducts are postulated as causes of this behaviour, and it is noted that Cu-$(phen)^+$ formally involves Cu^I. It is interesting to comment that no $Cu(acac)L^+$ was observed, and only a very weak peak ascribable to $Cu(tfac)L^+$, especially in the light of the spectral and structural discussions which follow. Whilst the Cu–acac or Cu–tfac interactions would involve stronger Cu–O bonds than in Cu–hfac, it appears that the species stabilised is that leading to the strongest Lewis acid.

The i.r. spectra of the ternary complexes show modifications over those of the binary complexes, CuA_2L (see Table 2). It is possible to suggest structures for the ternary complexes by referring to the carbonyl stretching frequency (*ca.* 1 650 cm^{-1}), the ring deformation [13] (*ca.* 660 cm^{-1}), and the CF_3 deformation [13] (*ca.* 580 cm^{-1}) of the hexafluoroacetylacetonate.[7] The presence of bands at *ca.* 658 and *ca.* 570 cm^{-1} indicates that the Cu(acac)(hfac) species all contain an ' ionic ' or weakly co-ordinated $hfac^-$, as does also the dark green form of Cu(tfac)(hfac)-(bipy). The spectra of the remaining Cu(tfac)(hfac) complexes show close similarity, in this region, to the spectra of known *cis*-octahedral $Cu(hfac)_2L$ species. This pattern is further reflected in the carbonyl stretching frequencies, although interpretation of the assignments is less clear cut.

All species show a weakening of the Cu–O bond on complexation as is evidenced by the movement of the carbonyl stretching frequency to higher frequency than that observed in the parent compound. This trend parallels that observed for $Cu(hfac)_2$ and $Cu(tfac)_2$ nitrogen-donor complexes.[4,7,14] In the Cu(acac)(hfac) series the effect is most clearly seen for Cu(acac)(hfac)(tmen) and $Cu(acac)(hfac)(phen)\cdot 2H_2O$ where shifts to 1 673 cm^{-1} occur, indicative of the presence of a free $hfac^-$. In Cu(acac)(hfac)(bipy) and Cu(acac)(hfac)(phen) similar, but smaller high-frequency shifts are observed suggesting a weakly associated, or a unidentate, $hfac^-$. For the Cu(tfac)(hfac) series the pattern is less clear: the light green bipy complex gives an unambiguous assignment as *cis* octahedral, and the dark green bipy complex shows the presence of an ionic $hfac^-$. The remaining complexes give high carbonyl stretching frequencies suggesting weakly bound $hfac^-$ and contrasting with the earlier assignment of *cis* octahedral.

Further evidence for structure assignment was found in the diffuse-reflectance spectra. The light green Cu-(tfac)(hfac)(bipy), Cu(tfac)(hfac)(tmen), and Cu(tfac)-(hfac)(phen)$\cdot H_2O$ all gave bands in the 770 nm region. This compares directly with the values obtained for genuine *cis*-octahedral complexes such as $Cu(hfac)_2$-(bipy) [4,15] and implies that these complexes have the same geometry. The high-frequency i.r. shift may be a reflection of the lowered π-acceptor properties of the bipy and tmen ligands relative to phen. The remaining complexes show diffuse reflectance bands in the 600—670 nm region. These complexes are bluish green

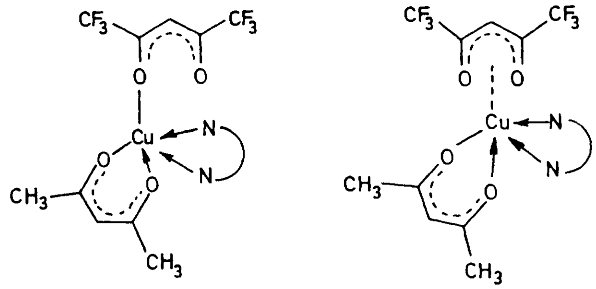
TABLE 2

Infrared and diffuse reflectance spectral data

Complex	I.r. (cm^{-1}) ν(C⩵O)	Ring deformation [a]	$\delta_{sym}(CF_3)$ [a]	Diffuse reflectance (nm)
$Cu(tfac)_2$	1 610			
$Cu(hfac)_2\cdot H_2O$	1 645			
Cu(acac)(hfac)	1 640			
$Cu(tfac)(hfac)\cdot H_2O$	1 640 (br)			
$Cu(tfac)_2(tmen)$	1 642			730
$Cu(hfac)_2(tmen)$	1 644	665 [a]	588 [a]	746
Cu(acac)(hfac)(tmen)	1 673	658	571	617
Cu(tfac)(hfac)(tmen)	1 672, 1 642	666	582, 572, 561	720
$Cu(tfac)_2(bipy)$	1 640			740
$Cu(hfac)_2(bipy)$	1 650	665 [a]		730
Cu(acac)(hfac)(bipy)	1 665	659	572	614
Cu(tfac)(hfac)(bipy) (light green)	1 655, 1 625	666	582	752
Cu(tfac)(hfac)(bipy) (dark green)	1 675, 1 620	659	572	645
$Cu(tfac)_2(phen)$	1 645			781
$Cu(hfac)_2(phen)$	1 645			740
Cu(acac)(hfac)(phen)	1 660	658	570	614
$Cu(acac)(hfac)(phen)\cdot 2H_2O$ [b]	1 673	658	572	625
$Cu(tfac)(hfac)(phen)\cdot H_2O$ [b]	1 660, 1 628	665	580, 575, 565	746

[a] Comparison is made with complexes of known structure (ref. 7). The complexes $Cu(hfac)_2(bipy)$ and $Cu(hfac)_2(tmen)$ are *cis* octahedral; $[Htmnd][Cu(hfac)_3]$ (672, 589 cm^{-1}) is octahedral; $Cu(hfac)_2(dmen)_2$ (659, 570 cm^{-1}) has unidentate $hfac^-$, and [Htmnd]-[hfac] (658, 573 cm^{-1}) has ionic $hfac^-$ present (tmnd = *NNN'N'*-tetramethylnaphthalene-1,8-diamine; dmen = *NN*-dimethylethane-1,2-diamine). [b] Water bands at 3 440 (br) and 1 640 cm^{-1}, br = broad.

to dark green in colour, contrasting with the light green of the *cis*-octahedral complexes and comparable with those observed for the mixed species Cu(tmen)(β-diketonate)X (β-diketonate = acac, tfac, or hfac; X = ClO_4 or NO_3).[16] In these complexes $\nu_{max.}$ values were of a similar range to our ternary complexes



C D

and followed two trends; (I) $ClO_4 > NO_3$ and (II) hfac < tfac < acac, the order of σ-donating power of the oxygen-donor atoms. The perchlorates were found to interact with the metal only for the hfac species in which splittings of the anion band in the i.r. were observed. It was suggested also that for the nitrates

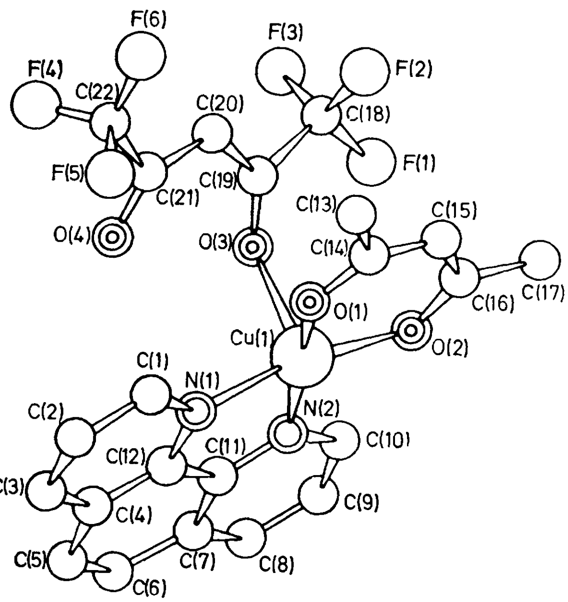


FIGURE 1 Molecular geometry and atomic labelling of Cu(acac)(hfac)(phen)

some interionic interactions, probably weak co-ordination of the anion to the metal, occurred.

Our data are limited but it is possible to extend the series (I) to include hfac⁻ for the species Cu(acac)(tmen)X. This gives the order $ClO_4^- > NO_3^- >$ hfac⁻ for $\nu_{max.}$ and if this is a reflection of the weak anionic interaction at the metal, the suggestion that hfac⁻ has some interaction with the metal may be made. This is also substantiated by the observation that in Cu(hfac)(tmen)ClO_4 the carbonyl stretching frequency is at 1 655 cm^{-1},[16] suggesting strong chelation of hfac in contrast to the ionic hfac in Cu(acac)(hfac)(tmen). Therefore we may formulate our species as [Cu(acac)L][hfac].

Given this formulation it is possible to propose two structures (C and D) for the ternary complexes of this type. In C a unidentate hfac⁻ is present, but having a delocalised structure, no i.r. evidence being present for an uncomplexed carbonyl group; in D a weakly co-ordinated, or free, hfac⁻ is present. The shapes may be related to a *cis*-octahedral geometry in that a closer approach of the hfac⁻ to the metal would lead to such a structure. This provides a rationale for the high carbonyl stretching frequencies in the Cu(tfac)(hfac) complexes where the acceptor nature of the copper could be modified by the donor–acceptor properties of the chelate, leading to stronger or weaker hfac⁻ interaction and distortion, but not dissociation, of the octahedral species.

The slow recrystallisation of Cu(acac)(hfac)(phen) from

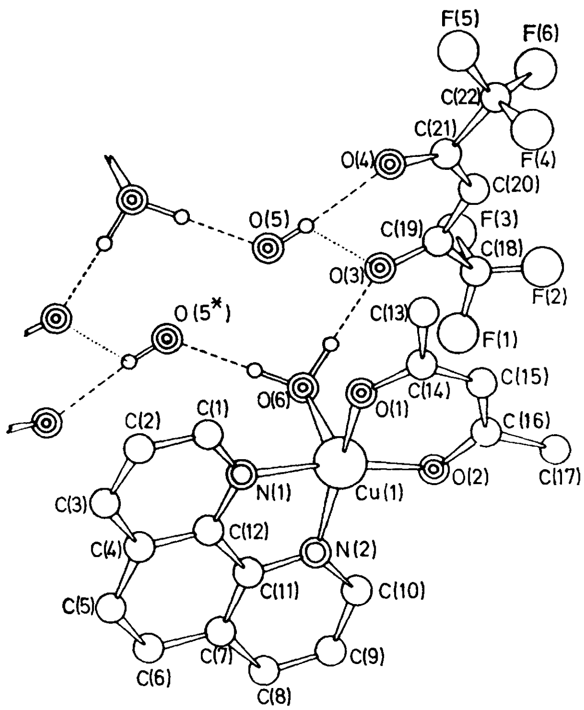


FIGURE 2 Molecular geometry, atomic labelling, and the hydrogen-bonding scheme of [Cu(acac)(phen)(OH_2)][hfac]·H_2O

toluene, or simply standing in the atmosphere followed by recrystallisation, leads to the isolation of Cu(acac)(hfac)(phen)·$2H_2O$. The above structures indicate modes of incorporation of water in which C could attract water through hydrogen bonding with the non-co-ordinated hfac oxygen atom and transfer it to the metal, and where in C and D the water molecule could be more strongly attracted to the copper than is the weakly interacting hfac.

In order to resolve the structural ambiguity *X*-ray analyses were carried out for Cu(acac)(hfac)(phen), (1), and for Cu(acac)(hfac)(phen)·$2H_2O$, (2).

The structures (1) and (2) are illustrated, along with atom labelling, in Figures 1 and 2; bond lengths and angles are compared in Table 3: important mean planes are detailed in Table 4. Both molecules contain a five-co-ordinate copper ion, complexed in a similar manner by a bidentate *o*-phenanthroline ligand and by an acetylacetonate ligand. In (1), the fifth co-ordination site is occupied, slightly asymmetrically, by a unidentate hexafluoroacetylacetonate ligand, whereas in (2), this fifth co-ordination site is occupied by a water molecule and the hexafluoroacetylacetonate species is present as the ion which is linked to the co-ordinated water molecule, and to a further unco-ordinated water molecule, by means of hydrogen bonds (see Figure 2).

The Cu(phen)(acac) fragments are almost identical in the two molecules, the only significant difference being the close coplanarity of the copper atom with the plane of the acac ligand in (2) (Table 4); in each molecule, the copper atom is displaced from the mean plane of the phen ligand by 0.13 Å. In both molecules, the copper atom is displaced by only 0.16 Å from the mean co-ordination plane defined by atoms N(1), N(2), O(1), and O(2); in each case, the displacement is towards the fifth ligand giving a flattened square-pyramidal co-ordination geometry for the copper ion. The unique copper–oxygen bond in each molecule is long, and slightly the longer to the hfac ligand in (1).

TABLE 3

Geometry of molecules (1) and (2) with estimated standard deviations in parentheses

(*a*) Bond lengths and other short contacts (Å)

	(1)	(2)
Cu(1)–O(1)	1.901(5)	1.916(4)
Cu(1)–O(2)	1.912(5)	1.904(3)
Cu(1)–N(1)	2.014(5)	2.008(4)
Cu(1)–N(2)	2.015(6)	2.009(5)
Cu(1)–O(3)	2.341(5)	
Cu(1)–O(6)		2.292(3)
N(1)–C(1)	1.332(10)	1.334(8)
N(2)–C(10)	1.328(10)	1.333(8)
N(1)–C(12)	1.356(9)	1.352(7)
N(2)–C(11)	1.344(8)	1.354(6)
C(1)–C(2)	1.407(11)	1.380(8)
C(9)–C(10)	1.424(12)	1.393(10)
C(2)–C(3)	1.359(13)	1.355(11)
C(8)–C(9)	1.359(13)	1.354(11)
C(3)–C(4)	1.412(12)	1.415(10)
C(7)–C(8)	1.403(11)	1.399(10)
C(4)–C(12)	1.398(10)	1.393(7)
C(7)–C(11)	1.418(10)	1.400(8)
C(4)–C(5)	1.438(12)	1.463(10)
C(6)–C(7)	1.441(11)	1.397(9)
C(5)–C(6)	1.334(12)	1.347(10)
C(11)–C(12)	1.420(10)	1.436(7)
O(1)–C(14)	1.278(10)	1.290(7)
O(2)–C(16)	1.287(10)	1.276(7)
C(14)–C(15)	1.380(13)	1.379(9)
C(15)–C(16)	1.386(14)	1.373(11)
C(13)–C(14)	1.507(14)	1.487(10)
C(16)–C(17)	1.517(14)	1.502(9)
O(3)–C(19)	1.235(9)	1.242(6)
O(4)–C(21)	1.224(10)	1.228(6)
C(19)–C(20)	1.395(11)	1.375(9)
C(20)–C(21)	1.410(12)	1.404(8)
C(18)–C(19)	1.614(8)	1.599(7)
C(21)–C(22)	1.611(9)	1.604(7)
O(3) · · · O(5)		3.00
O(4) · · · O(5)		2.83
O(3) · · · O(6)		2.77
O(6) · · · O(5 *)		2.76

TABLE 3 (*Continued*)

(*b*) Bond angles (°)

	(1)	(2)
N(1)–Cu(1)–N(2)	81.5(2)	82.0(2)
O(1)–Cu(1)–O(2)	95.1(2)	94.3(2)
N(1)–Cu(1)–O(1)	90.8(2)	91.7(2)
N(2)–Cu(1)–O(2)	90.9(2)	90.4(2)
N(1)–Cu(1)–O(2)	166.6(2)	169.9(2)
N(2)–Cu(1)–O(1)	168.9(2)	165.5(2)
N(1)–Cu(1)–O(ax.)	102.4(2)	93.4(1)
N(2)–Cu(1)–O(ax.)	91.3(2)	98.7(2)
O(1)–Cu(1)–O(ax.)	98.1(2)	94.6(2)
O(2)–Cu(1)–O(ax.)	88.7(2)	94.3(2)
Cu(1)–O(1)–C(14)	124.7(4)	124.6(3)
Cu(1)–O(2)–C(16)	123.2(4)	125.4(3)
O(1)–C(14)–C(13)	114.6(7)	114.6(5)
O(2)–C(16)–C(17)	114.1(7)	113.9(5)
O(1)–C(14)–C(15)	125.1(6)	124.9(4)
O(2)–C(16)–C(15)	125.8(6)	125.1(5)
C(13)–C(14)–C(15)	120.3(7)	120.5(5)
C(15)–C(16)–C(17)	120.1(7)	121.0(5)
C(14)–C(15)–C(16)	125.1(6)	125.7(5)
Cu(1)–O(3)–C(19)	124.6(4)	
O(3)–C(19)–C(18)	116.6(5)	113.4(4)
O(4)–C(21)–C(22)	114.3(6)	114.4(4)
O(3)–C(19)–C(20)	129.1(5)	129.7(4)
O(4)–C(21)–C(20)	129.3(5)	128.7(5)
C(18)–C(19)–C(20)	114.4(6)	116.8(3)
C(20)–C(21)–C(22)	116.4(5)	117.0(3)
C(19)–C(20)–C(21)	123.0(6)	124.0(4)
Cu(1)–N(1)–C(1)	128.1(3)	129.0(3)
Cu(1)–N(2)–C(10)	127.9(4)	128.9(3)
Cu(1)–N(1)–C(12)	112.6(3)	112.7(2)
Cu(1)–N(2)–C(11)	112.4(3)	112.5(2)
C(1)–N(1)–C(12)	119.1(5)	118.3(4)
C(10)–N(2)–C(11)	119.6(5)	118.5(4)
N(1)–C(1)–C(2)	120.5(5)	121.9(4)
N(2)–C(10)–C(9)	120.5(5)	121.4(4)
C(1)–C(2)–C(3)	120.5(7)	120.4(6)
C(8)–C(9)–C(10)	120.5(6)	120.3(6)
C(2)–C(3)–C(4)	120.1(6)	119.6(4)
C(7)–C(8)–C(9)	119.5(6)	120.1(5)
C(3)–C(4)–C(12)	116.0(5)	116.4(4)
C(8)–C(7)–C(11)	116.9(5)	116.6(4)
C(3)–C(4)–C(5)	124.9(5)	126.8(4)
C(6)–C(7)–C(8)	124.7(6)	124.3(5)
C(5)–C(4)–C(12)	119.1(5)	116.8(4)
C(6)–C(7)–C(11)	118.4(6)	119.1(5)
C(4)–C(5)–C(6)	121.1(5)	122.0(4)
C(5)–C(6)–C(7)	121.4(5)	121.3(5)
N(1)–C(12)–C(4)	123.7(5)	123.5(3)
N(2)–C(11)–C(7)	123.0(5)	123.2(4)
N(1)–C(12)–C(11)	116.0(4)	116.2(3)
N(2)–C(11)–C(12)	117.2(5)	116.4(4)
C(4)–C(12)–C(11)	120.3(6)	120.3(4)
C(7)–C(11)–C(12)	119.8(5)	120.5(4)

O(ax.) corresponds to O(3) for molecule (1), and to O(6) for molecule (2).

* Represents atom related by symm operation 1 − *x*, −*y*, 1 − *z*.

The skeleton of the free hfac anion [in molecule (2)] is planar and has an unexceptionable geometry with no evidence of π-bond localisation. The co-ordinated hfac ligand [in molecule (I)] is considerably less planar (see Table 4), being best referred to two planes having the γ-carbon atom in common. The length of the carbon–oxygen bond involving the co-ordinated oxygen atom [O(3) of molecule (1)] is not significantly longer than the three terminal carbon–oxygen bonds of the hfac ligands and the copper atom in no way approaches the plane of the co-ordinated hfac ligand. The consistently long carbon–carbon (trifluoromethyl) bond lengths (mean

TABLE 4

Equations of important least-squares planes for molecules (1) and (2) [X, Y, and Z are atomic co-ordinates (Å) referred to the mutually perpendicular axes a, b,* c']. Deviations (Å) of various atoms from these planes are given in parentheses

Plane (i): O(1), O(2), N(1), N(2)

Molecule (1)

$$-0.2585X - 0.4872Y - 0.8342Z = -1.705$$

[Cu(1) −0.173, O(1) −0.024, O(2) 0.024, N(1) 0.025, N(2) −0.025]

Molecule (2)

$$-0.2637X - 0.0895Y - 0.9605Z = -1.773$$

[Cu(1) −0.177, O(1) 0.050, O(2) −0.051, N(1) −0.053, N(2) 0.054]

Plane (ii): N(1), N(2), C(1)—C(12)

Molecule (1)

$$0.2617X + 0.4536Y + 0.8519Z = 1.697$$

[Cu(1) 0.126, N(1) 0.003, N(2) 0.001, C(1) 0.023, C(2) −0.008, C(3) −0.007, C(4) −0.013, C(5) 0.009, C(6) 0.022, C(7) −0.011, C(8) 0.000, C(9) −0.001, C(10) 0.005, C(11) −0.015, C(12) −0.009]

Molecule (2)

$$0.2090X + 0.0783Y + 0.9748Z = 1.714$$

[Cu(1) 0.141, N(1) 0.028, N(2) 0.026, C(1) −0.001, C(2) −0.049, C(3) −0.034, C(4) 0.008, C(5) 0.036, C(6) 0.020, C(7) −0.002, C(8) −0.040, C(9) −0.041, C(10) 0.005, C(11) 0.021, C(12) 0.025]

Plane (iii): O(1), O(2), C(14)—C(16)

Molecule (1)

$$0.2397X + 0.4789Y + 0.8445Z = 1.639$$

[Cu(1) 0.201, O(1) 0.010, O(2) −0.004, C(13) −0.079, C(14) −0.016, C(15) 0.011, C(16) −0.000, C(17) −0.048]

Molecule (2)

$$0.3531X + 0.1615Y + 0.9216Z = 2.127$$

[Cu(1) 0.029, O(1) 0.004, O(2) −0.002, C(13) −0.057, C(14) −0.006, C(15) 0.004, C(16) 0.000, C(17) −0.016]

Plane (iv): O(3), O(4), C(19)—C(21)

Molecule (1)

$$-0.1371X + 0.1577Y + 0.9779Z = 2.745$$

[Cu(1) −2.031, O(3) −0.043, O(4) 0.048, C(18) 0.317, C(19) 0.051, C(20) 0.004, C(21) −0.059, C(22) −0.312]

Molecule (2)

$$0.3905X - 0.0549Y + 0.9190Z = 4.996$$

[O(3) −0.004, O(4) 0.007, C(18) 0.093, C(19) 0.003, C(20) 0.005, C(21) −0.010, C(22) −0.082]

Plane (v): O(3), C(18)—C(20)

Molecule (1)

$$0.1242X - 0.0009Y - 0.9923Z = -2.219$$

[O(3) −0.004, O(4) −0.420, C(18) −0.003, C(19) 0.011, C(20) −0.004, C(21) −0.155, C(22) 0.052]

Plane (vi): O(4), C(20)—C(22)

Molecule (1)

$$0.0212X + 0.1699Y + 0.9852Z = 3.469$$

[O(3) −0.420, O(4) −0.000, C(18) 0.062, C(19) −0.154, C(20) −0.000, C(21) 0.001, C(22) −0.000]

Selected interplanar angles (°)

177.8	(i)—(ii)	176.7
178.7	(i)—(iii)	173.0
2.0	(ii)—(iii)	10.0
167.2	(v)—(vi)	

Both *o*-phenanthroline ligands are slightly buckled [planes (ii)] and, in each molecule, all six-membered ring fragments are closely planar (maximum root-mean-square deviation 0.011 Å).

value 1.607 Å) clearly suggest that a modified model for the constrained geometry of the trifluoromethyl groups might have been an improvement, with longer carbon–fluorine bonds and/or reduced F–C–F angles but it was considered that further elaboration of the model was not justified.

From consideration of the short oxygen–oxygen contacts in (2) (see Table 3), a hydrogen-bonding scheme is proposed in which the two hydrogen atoms of the co-ordinated water molecule form hydrogen bonds to one of the oxygen atoms of an hfac anion and to an unco-ordinated water molecule: a symmetry-related unco-ordinated water molecule forms a further hydrogen bond to the second oxygen atom of the anionic hfac species. The remaining hydrogen atom of the unco-ordinated water molecule is disordered over the two remaining tetrahedral sites. Thus, the 3.00 Å O(3) · · · O(5) contact of Table 3 is regarded as not significant.

EXPERIMENTAL

Infrared spectra were recorded as Nujol mulls or KBr discs using a Perkin-Elmer 457 grating instrument, and diffuse-reflectance spectra were recorded using a Cary 14 spectrometer. Microanalyses were by Miss M. A. McKinnon of these laboratories.

The mixed β-diketonate complexes, Cu(acac)(tfac), Cu(acac)(hfac), and Cu(hfac)(tfac) were prepared by the method of Farona *et al.*[1] The ternary complexes were prepared by application of the general method of ref. 4. Stoicheiometric amounts of the mixed β-diketonate and the required ligand were warmed together in dichloromethane, benzene, or toluene and the product recrystallised from the same solvents.

Determination of the Crystal Structures.—Molecule (1). Crystal data: $C_{22}H_{16}CuF_6N_2O_4$, $M = 549.91$, Triclinic, $a = 12.623(6)$, $b = 11.470(6)$, $c = 8.111(32)$ Å, $\alpha = 81.17(4)$, $\beta = 92.484(8)$, $\gamma = 97.691(4)°$, $U = 1\,150(5)$ Å^3, $D_m = 1.57$, $Z = 2$, $D_c = 1.587$ g cm^{-3}, space group $P\bar{1}$ (C_i, no. 2) assumed and confirmed (Delaunay reduced unit cell $a = 15.879$, $b = 12.911$, $c = 8.111$ Å, $\alpha = 119.26$, $\beta = 94.38$, $\gamma = 119.74°$ not used in analysis), $F(000) = 554$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 10.28 cm^{-1}. Three-dimensional X-ray diffraction data with $6.5 < 2\theta < 50°$ were collected from a crystal of mean dimensions $0.05 \times 0.08 \times 0.60$ mm mounted along the c axis on a Stoe Stadi-2 X-ray diffractometer, using graphite-monochromated Mo-K_α X-radiation, by the rotating-crystal, stationary-counter technique. Background counts were measured for each reflection at each extremity of a variable-width scan and data with $I/\sigma(I) > 3.0$, comprising 2 470 independent reflections, were accepted for use in the structure analysis and were corrected for Lorentz, polarisation, and absorption effects. The structure was solved by conventional Patterson and Fourier methods, the fluorine electron density being rather diffuse, and refined by block-diagonal least-squares methods to R 0.123, allowing thermal anisotropy for all non-hydrogen atoms with the exception of those of the trifluoromethyl groups. At this stage, a difference electron-density synthesis showed further electron density in the annulus defined by three fluorine atoms of each trifluoromethyl group, at positions between the already inserted fluorine atoms. It seemed that this density could be best expressed in terms of a disorder of the fluorine atoms rather than merely as high thermal vibration; consequently, constrained-geometry (C–F 1.28 Å, as surveyed from ref. 17; tetrahedral angles at the carbon atoms), disordered trifluoromethyl groups were positionally refined, along with an overall isotropic thermal parameter and a disorder population parameter for each group. At the completion of refinement of disorder parameters [0.620 : 0.380 for F(1)—F(3); 0.608 : 0.392 for F(4)—F(6)] at R 0.087, thermal anisotropy was introduced for the major disorder component only and for the carbon atoms of the trifluoromethyl groups. A difference electron-density synthesis revealed all hydrogen atoms with the exception of those of the methyl groups; these were accounted for by a disorder of six, half-population hydrogen atoms distributed around the annulus (on which the difference electron-density synthesis showed unresolved low electron density). Hydrogen atoms were included in structure-factor calculations (with B = 7.0 Å^2) but were not refined. After allowance for the anomalous scattering of the copper atom, refinement converged at R 0.0646. Atomic scattering factors were taken from ref. 18; unit weights were used throughout the refinement. Atomic positional parameters, together with estimated standard deviations, are listed in Table 5.

TABLE 5

Atomic positional parameters with estimated standard deviations in parentheses for molecule (1)

Atom	x/a	y/b	z/c
Cu(1)	0.136 71(7)	0.184 54(8)	0.034 96(12)
O(1)	0.271 9(4)	0.196 4(5)	−0.065 1(6)
O(2)	0.092 4(4)	0.320 1(4)	−0.104 8(6)
O(3)	0.187 7(4)	0.305 2(4)	0.240 3(6)
O(4)	0.344 4(5)	0.142 2(5)	0.360 1(8)
N(1)	0.154 5(4)	0.021 0(5)	0.155 8(7)
N(2)	−0.011 1(4)	0.140 2(5)	0.128 3(7)
C(1)	0.241 2(6)	−0.034 7(7)	0.166 9(10)
C(2)	0.241 1(7)	−0.147 4(7)	0.264 0(11)
C(3)	0.154 0(8)	−0.199 2(7)	0.353 1(10)
C(4)	0.061 5(6)	−0.141 5(6)	0.345 0(9)
C(5)	−0.034 4(7)	−0.186 8(7)	0.435 6(10)
C(6)	−0.117 9(7)	−0.125 6(7)	0.422 9(10)
C(7)	−0.116 3(6)	−0.012 9(7)	0.315 7(9)
C(8)	−0.200 8(6)	0.056 4(8)	0.295 8(11)
C(9)	−0.189 2(6)	0.162 8(8)	0.194 0(11)
C(10)	−0.091 7(6)	0.204 9(7)	0.109 7(10)
C(11)	−0.022 0(5)	0.034 1(6)	0.226 9(8)
C(12)	0.067 0(6)	−0.030 9(6)	0.243 2(8)
C(13)	0.423 3(8)	0.276 5(12)	−0.222 4(14)
C(14)	0.311 6(7)	0.284 2(8)	−0.170 4(10)
C(15)	0.260 2(7)	0.380 6(8)	−0.235 4(11)
C(16)	0.155 9(8)	0.393 8(7)	−0.202 9(10)
C(17)	0.106 3(10)	0.500 9(9)	−0.289 9(15)
C(18)	0.258 6(4)	0.515 1(3)	0.205 0(7)
C(19)	0.271 1(6)	0.375 2(6)	0.239 5(9)
C(20)	0.376 3(6)	0.350 7(7)	0.266 3(11)
C(21)	0.403 0(6)	0.234 9(8)	0.317 1(10)
C(22)	0.528 2(3)	0.220 1(6)	0.319 3(8)
F(1)	0.165 4(5)	0.528 0(6)	0.141 9(14)
F(2)	0.329 6(7)	0.573 5(6)	0.105 5(12)
F(3)	0.268 9(9)	0.554 2(6)	0.345 1(7)
F(11)	0.343 8(5)	0.575 8(6)	0.253 0(14)
F(12)	0.179 6(7)	0.530 3(6)	0.289 5(12)
F(13)	0.240 4(9)	0.549 6(6)	0.049 9(7)
F(4)	0.552 4(6)	0.155 0(11)	0.454 8(12)
F(5)	0.544 4(6)	0.169 1(11)	0.194 5(11)
F(6)	0.586 4(6)	0.321 3(6)	0.307 6(17)
F(14)	0.569 7(6)	0.275 2(11)	0.183 3(12)
F(15)	0.577 7(6)	0.261 1(11)	0.443 5(11)
F(16)	0.535 8(6)	0.109 0(6)	0.330 4(17)

Atoms F(11)—F(16) represent the minor component of the CF_3 group disorder. The estimated standard deviations of the atoms of the CF_3 groups are estimated from those of the parameters associated with the refinement of the constrained groups.

Molecule (2). Crystal data. $C_{22}H_{20}CuF_6N_2O_6$, M = 585.94, Triclinic, a = 12.284(6), b = 14.437(7), c = 8.020(8) Å, α = 78.417(13), β = 109.315(21), γ = 113.073(7)°, U = 1 230.7(15) Å^3, D_m = 1.56, Z = 2, D_c = 1.580 g cm^{-3}, space group $P\bar{1}$ (C_i, no. 2) assumed and confirmed (Delaunay reduced unit cell a = 14.843, b = 14.437, c = 8.020 Å, α = 101.58, β = 94.50, γ = 130.41° not used in the analysis), $F(000)$ = 594, Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 9.7 cm^{-1}. Data were collected (crystal dimensions 0.20 × 0.25 × 0.40 mm) and corrected (3 583 independent reflections) and the structure was solved as for molecule (1). In this case, only one trifluoromethyl group was found to be disordered [refined parameter 0.639 : 0.361 for F(4)—F(6)]. One hydrogen atom of an unco-ordinated water molecule appeared to be equally disordered over two geometrically acceptable sites (see Figure 2). Refinement as for molecule (1) converged at R 0.0546. Atomic positional parameters, together with estimated standard deviations, are listed in Table 6.

TABLE 6

Atomic positional parameters with estimated standard deviations in parentheses for molecule (2)

Atom	x/a	y/b	z/c
Cu(1)	0.232 30(5)	0.100 04(4)	0.171 10(8)
O(1)	0.361 5(3)	0.118 1(3)	0.070 8(5)
O(2)	0.248 0(4)	0.238 6(3)	0.128 5(5)
O(3)	0.590 4(3)	0.248 3(3)	0.446 0(5)
O(4)	0.774 1(3)	0.240 3(2)	0.296 3(6)
O(5)	0.593 2(4)	0.054 8(3)	0.366 4(6)
O(6)	0.357 1(3)	0.115 6(2)	0.456 4(4)
N(1)	0.184 5(3)	−0.050 9(3)	0.192 7(5)
N(2)	0.069 7(3)	0.063 5(3)	0.220 2(5)
C(1)	0.244 3(5)	−0.106 0(4)	0.173 3(7)
C(2)	0.200 0(6)	−0.210 1(4)	0.196 9(8)
C(3)	0.094 6(6)	−0.259 7(4)	0.245 5(8)
C(4)	0.028 7(5)	−0.204 2(4)	0.269 0(6)
C(5)	−0.085 6(6)	−0.245 2(5)	0.321 5(8)
C(6)	−0.143 7(5)	−0.185 6(5)	0.333 0(8)
C(7)	−0.096 0(4)	−0.080 9(5)	0.297 9(6)
C(8)	−0.152 3(5)	−0.014 7(6)	0.304 7(7)
C(9)	−0.098 2(5)	0.086 0(6)	0.270 6(7)
C(10)	0.014 0(5)	0.124 3(4)	0.229 9(7)
C(11)	0.015 6(4)	−0.037 3(4)	0.253 4(5)
C(12)	0.078 3(4)	−0.099 6(3)	0.238 8(6)
C(13)	0.519 2(6)	0.197 9(7)	−0.067 7(9)
C(14)	0.426 1(5)	0.203 5(5)	0.006 5(6)
C(15)	0.412 3(6)	0.294 5(5)	0.000 9(8)
C(16)	0.326 8(6)	0.308 3(4)	0.059 1(7)
C(17)	0.318 7(8)	0.411 0(5)	0.042 8(11)
C(18)	0.610 6(3)	0.411 6(2)	0.499 4(4)
C(19)	0.652 4(5)	0.339 3(4)	0.426 6(7)
C(20)	0.752 9(5)	0.384 8(3)	0.360 5(7)
C(21)	0.804 5(5)	0.331 9(4)	0.298 9(7)
C(22)	0.917 2(3)	0.398 1(2)	0.217 0(5)
F(1)	0.495 1(4)	0.372 0(3)	0.485 9(6)
F(2)	0.633 8(4)	0.498 5(3)	0.412 8(6)
F(3)	0.671 3(4)	0.421 4(3)	0.662 9(5)
F(4)	0.872 2(5)	0.418 5(5)	0.051 5(6)
F(5)	0.987 3(4)	0.348 1(3)	0.237 0(9)
F(6)	0.979 8(5)	0.480 4(4)	0.292 9(8)
F(14)	1.020 6(5)	0.412 8(5)	0.336 0(6)
F(15)	0.905 6(4)	0.483 2(3)	0.150 5(9)
F(16)	0.913 0(5)	0.350 9(4)	0.094 6(8)

Atoms F(14)—F(16) represent the minor component of the CF_3 group disorder. The estimated standard deviations of the atoms of the CF_3 groups are estimated from those of the parameters associated with the refinement of the constrained groups.

Tables of observed structure amplitudes and calculated structure factors, hydrogen-atom co-ordinates, and anisotropic thermal parameters, for both structures, are deposited in Supplementary Publication No. SUP 22718 (60 pp.).*

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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