The Coordinative Saturation of Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)-iron(II) and the Crystal Structure of a Related Bimetallic Copper(II) Complex

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Complexes of bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)iron(II) with bidentate-N-containing ligands (1,2-diaminoethane; N,N-dimethyl-1,2-diaminoethane; N,N′-dimethyl-1,2-diaminoethane; 1,10-phenanthroline; 2,2′-bipyridyl), the 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato anion, tri- and tetradentate N-containing ligands (N-2-dimethyl-aminoethyl-N,N′,N′-trimethyl-1,2-diaminoethane; N,N′-bis(2-methylaminoethyl-N,N′-dimethyl)-1,2-diaminoethane), tetradentate macrocyclic ligands (5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradecane; 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetra-decane) and tetradentate metal Schiff base complexes (based on salen and acen) have been prepared and their spectral and chemical properties investigated.

The crystal structure of $[Cu(hfpd)_2]_2$ (trien-Me_6) is monoclinic, space group $P2_1/a$; *two $[Cu(hfpd)_2]$ units are bridged by the (trien-Me_6) ligand and the whole binuclear molecule possesses crystallographically imposed inversion symmetry.*

Introduction

The coordinative saturation of metal(II) β-diketonates may be achieved through addition of Lewis bases [1]; progressive trifluoromethylation of the β-diketone enhances the affinity of the central metal atom for ligation [2]. As part of an investigation into the use of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hhfpd) to help achieve coordinative saturation in divalent β-diketonate complexes we report here the interaction of $Fe(hfpd)_2$ with a wide range of polydentate donor ligands, with $hfpd^-$, and with some metal(II) Schiff base complexes. The crystal structure of the related homobinuclear copper(II) complex $[Cu(hfpd)_2]_2$ trien-Me_6 (trien-Me_6 = N,N′-bis(dimethylaminoethyl-N,N′-dimethyl)-1,2-diaminoethane) is also reported together with some new $Cu(hfpd)_2$ complexes containing polydentate ligands. The structure provides a unique example of the binucleating capability of the tetramine.

Results and Discussion

$Fe(hfpd)_2,2H_2O$ was prepared according to the literature method. Bis-monodentate complexes of $Fe(hfpd)_2$ have also been reported with thf [7], EtOH [7], pyridine [8], and tributylphosphine oxide [9] as the ligands and these, together with the hydrate, clearly indicate the achievement of coordinative saturation of the Fe(II) through ligation. Consequently $Fe(hfpd)_2,2H_2O$ was reacted with a series of polydentate ligands and coordinatively saturated complexes prepared in which the two molecules of water have been exchanged with donors from the incoming ligand.

Bidentate N-Containing Ligands

The complexes $Fe(hfpd)_2$,L (L = 1,2-diaminoethane(en), N,N-dimethyl-1,2-diaminoethane (asym-dmen), N,N′-dimethyl-1,2-diaminoethane (sym-dmen), N,N,N′,N′-tetramethyl-1,2-diaminoethane (tmen), 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) were prepared by reaction of $Fe(hfpd)_2$, $2H_2O$) with the appropriate ligand in stoichieometric amount in ethanol or toluene. It was necessary to prepare the en complex by use of vacuum line techniques. The complexes are all maroon in colour and sufficiently stable to be handled in the atmosphere—presumably their six-coordinated nature restricts pathways to oxidation. The disappearance of the band *ca.* 3,400 cm^{-1}, ascribed to coordinated water in $Fe(hfpd)_2,2H_2O$, indicates that chelation has occurred and the IR spectra of the iron(II) complexes are all comparable with those found for the corresponding copper(II) complexes [3]. The $\nu_{C=O}$ band occurs in the 1630 cm^{-1} region (Table I). It is most likely that the complexes are *cis*-octahedral in nature; $Cu(hfpd)_2$, bipy has been shown to have this geometry by X-ray crystallographic studies [10].

Mössbauer spectra of representative complexes are typical of high spin, six-coordinated iron(II) complexes [11] (Table II); an asymmetry of the doublet is observed as in the spectrum of $Fe(hfpd)_2,2H_2O$ where it was attributed to a texture effect resulting from the shape of the microcrystals [12]. Mass spectra showed the presence of the parent ion,

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TABLE I. Microanalytical Data and Selected IR Bands (cm^{-1}).

	Found %			Required %			$\nu_{C=O}$	NH
	C	H	N	C	H	N		
Iron Complexes								
$Fe(hfpd)_2,2H_2O$	22.9	1.0		23.7	1.2		1630	
$Fe(hfpd)_2$,en	27.5	2.2	5.5	27.3	1.5	5.3	1630	3380, 3300 3160
$Fe(hfpd)_2$, asym-dmen	30.9	2.6	5.2	30.1	2.5	5.1	1630	3300, 3360 3350, 3310
$Fe(hfpd)_2$,sym-dmen	30.0	2.5	5.2	30.1	2.5	5.1	1630	3310, 3120
$Fe(hfpd)_2$,tmen	32.6	3.1	4.5	32.7	3.1	4.7	1630	
$Fe(hfpd)_2$,phen	41.0	1.2	4.3	40.6	1.5	4.4	1630	
$Fe(hfpd)_2$,bipy	38.2	1.7	4.5	38.3	1.6	4.5	1630	
$[tmndH]^+[Fe(hfpd)_3]^-$	39.4	2.5	3.1	39.0	2.5	3.1	1630	
$Fe(hfpd)_2$,dien-Me_5	36.0	3.8	6.6	35.5	3.9	6.5	1665 m, 1630 s	
$Fe(hfpd)_2$,trien-Me_6	37.6	4.1	8.2	37.7	4.6	8.0	1670 s, 1630 s	
$Fe(hfpd)_2,Mc^1$	48.3	3.9	6.7	48.0	4.5	6.6	1670 sh, 1650 s	3180
$Fe(hfpd)_2,Mc^2$	48.2	4.2	6.5	48.2	4.0	6.6	1665 s	3200
$Fe(hfpd)_2,Mc^3$	41.7	4.9	7.1	41.4	5.0	7.4	1670 s	3200
$Fe(hfpd)_2$,Cu(salen)	40.6	2.9	4.0	39.0	2.0	3.5	1635	
$Fe(hfpd)_2$,Ni(salen)	39.4	2.3	3.7	39.2	2.0	3.5	1630	
$Fe(hfpd)_2$,Co(salen)	40.6	2.3	3.9	39.2	2.0	3.5	1640	
$Fe(hfpd)_2$,Cu(acen)	34.6	2.6	3.5	34.9	2.6	3.7	1640	
$Fe(hfpd)_2$,Ni(acen)	35.5	2.6	3.6	35.2	2.7	3.7	1635	
$[Fe(hfpd)_2]_2$,trien-Me_6	32.8	2.9	4.7	32.8	2.9	4.8	1630	
Fe(hfpd),salen,H_2O	46.3	2.8	4.9	46.1	3.1	5.1	1650, 1635	
Copper Complexes								
$Cu(hfpd)_2$,dien-Me_5	35.7	3.9	6.8	35.1	3.8	6.5	1670, 1650	
$Cu(hfpd)_2$,trien-Me_6	37.3	5.1	8.0	37.4	4.5	7.9	1670	
$[Cu(hfpd)_2]_2$,trien-Me_6	32.9	2.9	5.1	32.4	2.8	4.7	1650	
$Cu(hfpd)_2, Mc^1$	48.2	3.8	6.4	48.0	3.7	6.7	1660	3140
$Cu(hfpd)_2,Mc^2$	48.3	4.9	6.7	47.6	4.0	6.5	1660	3260, 3130
$Cu(hfpd)_2,Mc^3$	41.1	5.1	7.6	41.0	5.2	7.4	1670	3200, 3140

$[Fe(hfpd)_2L]^+$ (Table III). Izumi *et al.* [13] have studied the fragmentation pattern of the base adducts $(hfpd_2)M,L$ (M = Cu(II), Co(II), Zn(II) and Ni(II); L = phen and bipy). They observed that the pattern for $Co(hfpd)_2$,phen and the Ni(II) adducts was initiated *via* loss of one $hfpd^-$ group, whereas for the remaining species the initial loss was of CF_3^-, followed by either base or $CF_3COCHCO^-$. This indicated that the nitrogeneous bases are held more firmly by the metal ion in the former group. In the series $Fe(hfpd)_2,L$ the m.s. show three alternative pathways: (a) initial loss of fluoride, (b) initial loss of $(hfpd)^-$ and (c) initial loss of L. As the bidentate ligands and $(hfpd)^-$ are lost indiscriminately it can be assumed that they are bonded to the metal with similar strength. During the course of this work a complex of $Fe(hfpd)_2$ with tmen was reported, together with its properties as a potential anti-knocking agent for petrol [14].

1,1,1,5,5,5-Hexafluoropentane-2,4-dionate, $(hfpd)^-$, as a Ligand

The reaction of $[tmndH^+][hfpd^-]$, ($tmndH^+$ = monoprotonated N,N,N′,N′-tetramethyl-1,8-naphthalenediamine), with $Fe(hfpd)_2,2H_2O$ in 1:1 molar ratio in toluene gave $[tmndH^+][Fe(hfpd)_3^-]$ as a purple crystalline solid. Coordinative saturation has been here achieved through enolate addition. A single carbonyl band was found at 1630 cm^{-1} and an octahedral geometry assigned by comparison with the known structures of $[tmndH^+][Mg(hfpd)_3^-]$ and $[tmndH^+][Cu(hfpd)_3^-]$ [15, 16]. The Mössbauer spectrum is indicative of a high spin, six-coordinated iron(II), (Table II), and the m.s. showed $[Fe(hfpd)_2]^+$

TABLE II. Representative Mössbauer Spectral Parameters.

	I.S. (±0.03 mm/s)[c]	Q.S. (±0.06 mm)	T (K)
$Fe(hfpd)_2,2H_2O$	1.09	2.54	RT[a]
$Fe(hfpd)_2$,bipy	0.97	2.65	RT[a]
	1.23	3.07	77[a]
	1.04	2.70	RT[b]
$Fe(hfpd)_2$,phen	1.04	2.70	RT[b]
$Fe(hfpd)_2$,tmen	1.08	2.75	77[b]
$Fe(hfpd)_2$,trien-Me_6	1.08	2.70	RT[b]
$[Fe(hfpd)_2]_2$,trien-Me_6	1.02	2.74	RT[b]
$[tmndH]^+[Fe(hfpd)_3]^-$	1.16	2.55	RT[b]
$Fe(hfpd)_2$, Mc^3	1.13	2.99	RT[a]
	1.16	3.14	77[a]
$Fe(hfpd)_2$,Cu(salen)	1.13	2.59	RT[a]
	1.36	2.88	77[b]
	1.14	2.68	RT[a]
$Fe(hfpd)_2$,Ni(salen)	1.18	2.68	77[b]
$Fe(hfpd)_2$,Co(salen)	0.30	0.83	RT[a]
Fe(hfpd),salen,H_2O	0.43	0.96	RT[a]

[a] Velocity calibration *versus* S.N.P.; Source, Co/Rh. [b] Velocity calibration *versus* NBS Fe foil; Source Fe/Co. [c] All IS data is given *versus* Fe foil.

as the highest peak indicating the facile loss of $hfpd^-$ from the complex anion.

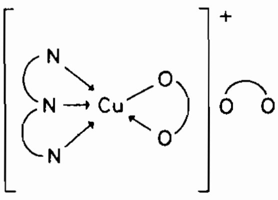
Tri- and Tetra-dentate Acyclic N-Containing Ligands

The reactions of $Fe(hfpd)_2,2H_2O$ with N-2-dimethylaminoethyl-N,N′,N′-trimethyl-1,2-diaminoethane (dien-Me_5) and N,N′-bis(2-dimethylaminoethyl-N,N′-dimethyl)-1,2-diaminoethane (trien-Me_6) were carried out; vacuum line techniques were employed as the reaction solutions were atmosphere sensitive. Dark maroon complexes having 1:1 stoicheiometry were isolated for both ligands, and if an excess of $Fe(hfpd)_2,2H_2O$ was used then the complex $[Fe(hfpd)_2]_2$trien-Me_6 could also be isolated.

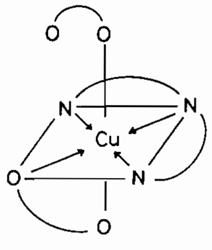
The IR spectrum of $Fe(hfpd)_2$dien-Me_5 shows two $\nu_{C=O}$ bands, one at 1665 cm^{-1} indicative of a 'loose' unidentate or ionic $hfpd^-$ [17], with a second band at 1630 cm^{-1} corresponding to a chelated $hfpd^-$ unit. Bands normally found between 2830 and 2760 cm^{-1}, arising from the >N-Me and -N(-Me)$_2$ moieties, are absent and this is indicative of coordination of the amine to the metal [18]. The 1:1 and 2:1 chelates of $Fe(hfpd)_2$ with trien-Me_6 do not show appreciable differences in their IR spectra apart from an additional band *ca.* 1670 cm^{-1} in the 1:1 adduct; both spectra have $\nu_{C=O}$ bands at 1630 cm^{-1}.

In order to attempt structural assignments the corresponding $Cu(hfpd)_2$ complexes were prepared as analogy could then be made with existing polydentate amino-complexes of copper(II) having present inorganic anions such as SCN^- and ClO_4^-. The IR of $Cu(hfpd)_2$dien-Me_5 showed two $\nu_{C=O}$ bands, at 1670 and 1650 cm^{-1}: that of $Cu(hfpd)_2$-trien-Me_6 gave one band at 1670 cm^{-1}. The IR of $[Cu(hfpd)_2]_2$trien-Me_6 gave one $\nu_{C=O}$ band at 1650 cm^{-1}.

X-ray crystallographic studies [19–21] show that dien-Me_5 coordinates to copper(II) such that, in the presence of monodentate anions, a distorted square pyramidal geometry is achieved with the ligand at the corners of the basal plane. In the complex [Cu(dien-Me_5)]$_2$[1,2,4,5-tetrahydroxybenzene], which utilises a chelating ligand, the coordination sphere at the metal is intermediate between trigonal bipyramidal and square pyramidal [22]. The structures (A) and (B) can be suggested as possibilities for $Cu(hfpd)_2$-(dien-Me_5) on the basis of the IR spectra and by analogy with the above.



(A)



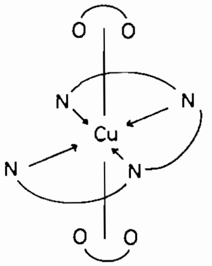
(B)

As the IR of $Fe(hfpd)_2$dien-Me_5 is closely similar to that of $Cu(hfpd)_2$dien-Me_5 these structures are also plausible for the Fe(II) complex.

TABLE III. M.S. of Iron Complexes.

$Fe(hfpd)_2en$	P^+	530
	$P^+ - F$	511
	$Fe(hfpd)_2^+$	470
	$Fe(hfpd)en^+$	323
$Fe(hfpd)_2$asym-dmen	P^+	558
	$P^+ - F$	539
	$Fe(hfpd)_2^+$	470
	$Fe(hfpd)L^+$	351
$Fe(hfpd)_2$sym-dmen	P^+	558
	$P^+ - F$	539
	$Fe(hfpd)_2^+$	470
	$Fe(hfpd)L^+$	351
$Fe(hfpd)_2tmen$	P^+	585
	$P^+ - F$	566
	$Fe(hfpd)_2^+$	470
	$Fe(hfpd)L^+$	379
$Fe(hfpd)_2phen$	P^+	650
	$P^+ - F$	631
	$Fe(hfpd)_2^+$	470
	$Fe(hfpd)L^+$	443
$Fe(hfpd)_2bipy$	P^+	626
	$P^+ - F$	607
	$Fe(hfpd)_2^+$	470
	$Fe(hfpd)L^+$	419
$Fe(hfpd)_2dien\text{-}Me_5$	P^+	643
	$P^+ - F$	625
	$Fe(hfpd)_2^+$	470
	$Fe(hfpd)L^+$	436
$Fe(hfpd)_2trien\text{-}Me_6$	P^+	700
	$P^+ - F$	681
	$Fe(hfpd)_2^+$	470
	$Fe(hfpd)L^+$	493
$[Fe(hfpd)_2]_2trien\text{-}Me_6$	$Fe(hfpd)_2L^+$	700
	$Fe(hfpd)_2^+$	470
$Fe(hfpd)_2Mc^1$	$P^+ - hfpd$	640
	$(Fe(hfpd)Mc^1 - F)^+$	621
	$(Fe(hfpd)Mc^1 - 2F)^+$	602
	$Fe(hfpd)_2^+$	470
	$(Fe - Mc^1 - F)^+$	451
	$(FeMc^1)$	433
$Fe(hfpd)_2Mc^2$	$P^+ - hfpd$	644
	$Fe(hfpd)_2^+$	470
	$(Fe - Mc^2)^+$	435
$Fe(hfpd)_2Mc^3$	$P^+ - hfpd$	547
	$Fe(hfpd)Mc^3 - CH_3)^+$	531
	$Fe(hfpd)^+$	470
	$(FeMc^3)^{+2}$	338
$[tmndH]^+[Fe(hfpd)_3]^-$	$Fe(hfpd)_2^+$	470
$Fe(hfpd)_2,Cu(salen)$	P^+	799
	$P^+ - F$	780
	$P^+ - 2F$	761
	$[Fe(hfpd),Cu(salen)]^+$	592
	$[Fe(hfpd)salen]^+$	529
	$[Fe(hfpd)salen - F]^+$	510
	$Fe(hfpd)_2^+$	470
	$Cu(salen)^+$	329
$Fe(hfpd)_2,Ni(salen)$	P^+	795
	$[Fe(hfpd)Ni(salen)]^+$	588
	$[Fe(hfpd)NL(salen) - F]^+$	569
	$Fe(hfpd)_2^+$	470
$Fe(hfpd)_2,Co(salen)$	P^+	795
	$[Fe(hfpd)(salen)]^+$	529
	$Co(hfpd)_2^+$	473
	$Fe(hfpd)^+$	470
	$[Co(hfpd)_2 - F]^+$	454
	$[Fe(hfpd)_2 - F]^+$	451
	$Co(salen)^+$	325
	$Fe(salen)^+$	322
$Fe(hfpd)_2,Cu(acen)$	P^+	756
	$P^+ - F$	737
	$[Fe(hfpd)Cu(acen)]^+$	549
	$[Fe(hfpd)acen]^+$	486
	$Fe(hfpd)_2^+$	470
	$Cu(acen)^+$	285
$Fe(hfpd)_2,Ni(acen)$	P^+	751
	$P^+ - F$	732
	$[Fe(hfpd)Ni(acen)]^+$	545
	$Fe(hfpd)_2$	470
	$Ni(acen)^+$	281

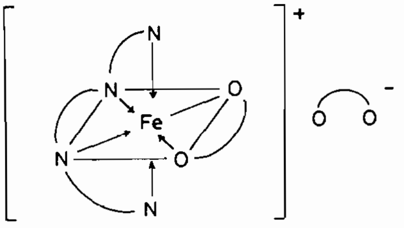
Complexes of the type $Cu(trien\text{-}Me_6)XY$ present similar physico-chemical properties [23] to those of $[Cu(trien)SCN]NCS$ for which an X-ray crystal structure has been solved [24]. This showed that the copper(II) is five-coordinated having the nitrogen donors of the tetraamine in the basal plane and one axial SCN^-. The IR of $Cu(hfpd)_2trien\text{-}Me_6$ gave only one carbonyl stretch at 1670 cm^{-1} and so the structure (C) is proposed for this compound—the (hfpd) anions are loosely held in the axial positions.



(C)

This may also be compared with the structure of $Cu(hfpd)_2(asym\text{-}dmen)_2$ in which the two diamines occupy the square plane and the (hfpd) anions the axial positions [17]. The $Fe(hfpd)_2$ complex of trien-

Me_6 however shows two (hfpd) anion environments, one chelated and one anionic. With one chelated anion present the tetraamine cannot take up four equatorial sites and so the structure (D) is proposed. The Mössbauer spectrum also indicates a high spin, octahedral Fe(II) environment.



(D)

For the 2:1 complexes involving trien-Me_6 the IR suggest that a single chelated hfpd anion environment is available, and the Mössbauer spectrum of the iron complex indicates high spin Fe(II) in an octahedral environment. A structure in which the trien-Me_6 acts as a homobinucleating ligand linking the two $Fe(hfpd)_2$ groups seemed most likely. Suitable crystals of this species were not available and so an X-ray crystal structure of the corresponding copper(II) complex $[(hfpd)_2Cu]_2$trien-Me_6 was carried out.

The structure of the dimeric molecule is illustrated in Fig. 1 with the atom labelling used in the corresponding Tables. Bond lengths and angles (together with estimated standard deviations) and details of planar fragments are given in Tables IV and V.

The molecule comprises a centrosymmetric dimer in which two $Cu(hfpd)_2$ units are bridged by a trien-Me_6 ligand. The copper coordination polyhedron is distorted octahedral with two, mutually *trans*, long copper–oxygen bonds, one to each (hfpd) ligand: the remaining four bonds show a small tetrahedral distortion away from square-planar coordination. The skeleton of each (hfpd) chelating ligand is approximately planar with minor deviations of the carbon atoms of the trifluoromethyl groups but substantial out-of-plane displacements of the copper atom. The (trien-Me_6) ligand chelates to each of the $[Cu(hfpd)_2]$ units by means of the terminal NCCN fragment; the whole dimeric molecule possesses crystallographically imposed inversion symmetry. The limited accuracy of the structural determination precludes any detailed discussion of the molecular geometry but bond lengths, bond angles and torsion angles within the ligands are unexceptionable.

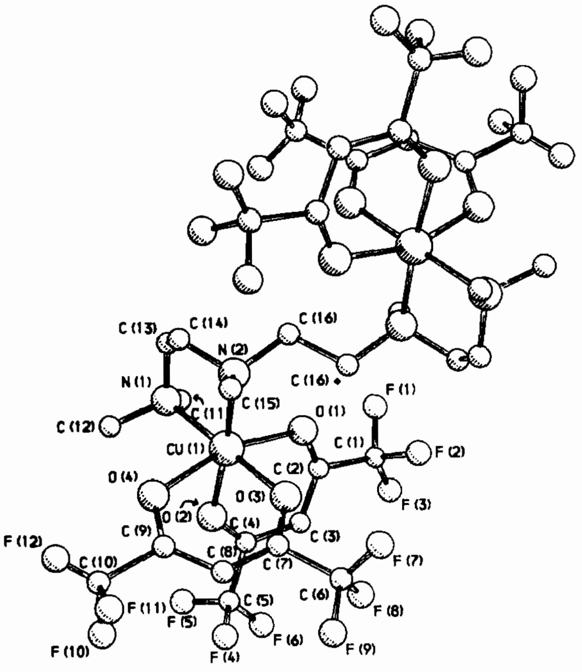
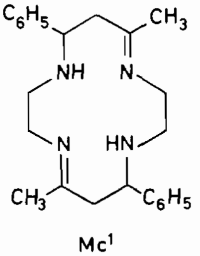


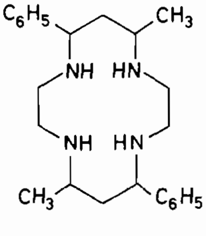
Fig. 1. The molecular structure of $[Cu(hfpd)_2]_2$trien-Me_6 with atom labelling of the asymmetric unit: atom C(16)* is centrosymmetrically related to atom C(16) through the crystallographic inversion centre at (0,0,0).

Tetradentate Macrocyclic Ligands

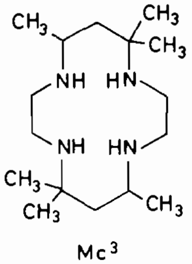
The reactions of $Fe(hfpd)_2,2H_2O$ with 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Mc^1), 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradecane (Mc^2) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Mc^3) were carried out under dry N_2 atmospheres to yield the complexes $Fe(hfpd)_2M$. The reactions were performed in this way as an extreme facility on the part of iron(II) to promote the oxidative dehydrogenation of the secondary amino groups bound to the metal has been found previously [25, 26].



Mc^1



Mc^2

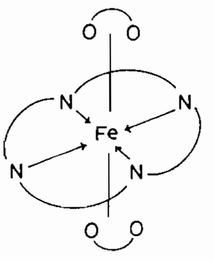


Mc^3

TABLE IV. Bond Lengths (Å) and Bond Angles (°) with Estimated Standard Deviations in parentheses for $[\mathrm{Cu(hfpd)_2}]_2\mathrm{trien\text{-}Me_6}$.

Cu(1)–O(1)	2.319(21)	O(1)–C(2)	1.19(3)
Cu(1)–O(2)	1.998(23)	C(1)–C(2)	1.61(3)
Cu(1)–O(3)	1.981(22)	C(2)–C(3)	1.41(4)
Cu(1)–O(4)	2.355(22)	C(3)–C(4)	1.44(5)
Cu(1)–N(1)	2.050(25)	C(4)–C(5)	1.50(4)
Cu(1)–N(2)	2.079(21)	O(2)–C(4)	1.25(4)
N(1)–C(11)	1.49(5)	O(3)–C(7)	1.23(4)
N(1)–C(12)	1.48(4)	C(6)–C(7)	1.57(4)
N(1)–C(13)	1.43(4)	C(7)–C(8)	1.37(5)
C(13)–C(14)	1.49(5)	C(8)–C(9)	1.41(4)
N(2)–C(14)	1.49(4)	C(9)–C(10)	1.56(3)
N(2)–C(15)	1.51(4)	O(4)–C(9)	1.20(3)
N(2)–C(16)	1.51(4)	C–F (all)	1.315
C(16)–C(16) *	1.51(5)		
O(1)–Cu(1)–O(2)	85.1(8)	Cu(1)–O(1)–C(2)	118.5(18)
O(1)–Cu(1)–O(3)	84.5(8)	C(2)–C(1)–F(1)	108.1(16)
O(1)–Cu(1)–O(4)	164.1(8)	C(2)–C(1)–F(2)	111.3(16)
O(1)–Cu(1)–N(1)	96.0(9)	C(2)–C(1)–F(3)	113.7(16)
O(1)–Cu(1)–N(2)	99.5(8)	O(1)–C(2)–C(1)	112.9(21)
O(2)–Cu(1)–O(3)	88.0(9)	O(1)–C(2)–C(3)	134.1(27)
O(2)–Cu(1)–O(4)	84.0(8)	C(1)–C(2)–C(3)	112.9(22)
O(2)–Cu(1)–N(1)	90.7(10)	C(2)–C(3)–C(4)	120.6(30)
O(2)–Cu(1)–N(2)	175.2(9)	C(3)–C(4)–C(5)	116.3(29)
O(3)–Cu(1)–O(4)	83.7(8)	O(2)–C(4)–C(3)	126.8(33)
O(3)–Cu(1)–N(1)	178.5(10)	O(2)–C(4)–C(5)	116.7(29)
O(3)–Cu(1)–N(2)	93.6(9)	C(4)–C(5)–F(4)	108.3(25)
O(4)–Cu(1)–N(1)	95.5(9)	C(4)–C(5)–F(5)	109.8(24)
O(4)–Cu(1)–N(2)	91.8(8)	C(4)–C(5)–F(6)	115.0(25)
N(1)–Cu(1)–N(2)	87.7(9)	Cu(1)–O(2)–C(4)	128.8(23)
Cu(1)–N(1)–C(11)	114.7(22)	Cu(1)–O(3)–C(7)	127.5(21)
Cu(1)–N(1)–C(12)	111.5(20)	C(7)–C(6)–F(7)	111.5(20)
Cu(1)–N(1)–C(13)	104.3(19)	C(7)–C(6)–F(8)	107.7(20)
C(11)–N(1)–C(12)	106.3(27)	C(7)–C(6)–F(9)	114.0(20)
C(11)–N(1)–C(13)	109.2(27)	O(3)–C(7)–C(6)	111.3(24)
C(12)–N(1)–C(13)	111.0(25)	O(3)–C(7)–C(8)	131.6(30)
N(1)–C(13)–C(14)	115.8(28)	C(6)–C(7)–C(8)	117.1(26)
N(2)–C(14)–C(13)	109.2(26)	C(7)–C(8)–C(9)	122.9(30)
Cu(1)–N(2)–C(14)	103.5(17)	C(8)–C(9)–C(10)	114.6(23)
Cu(1)–N(2)–C(15)	111.5(18)	O(4)–C(9)–C(8)	127.4(26)
Cu(1)–N(2)–C(16)	113.7(17)	O(4)–C(9)–C(10)	117.8(22)
C(14)–N(2)–C(15)	108.1(23)	C(9)–C(10)–F(10)	110.8(21)
C(14)–N(2)–C(16)	107.9(22)	C(9)–C(10)–F(11)	110.6(21)
C(15)–N(2)–C(16)	111.7(22)	C(9)–C(10)–F(12)	111.7(20)
N(2)–C(16)–C(16)*	112.4(25)	Cu(1)–O(4)–C(9)	119.3(18)
		F–C–F (all)	107.8

The complexes prepared give $\nu_{C=O}$ at 1665 cm^{-1} suggesting the presence of a monodentate or loosely bound hfpd$^-$; however the presence of weak bands at 1600 cm^{-1} make clear assignments more difficult than with the acyclic ligands (E). It is possible that there is some H-bonding between the free C–O group and the proximal NH from the macrocycle [17]. The Mössbauer parameters for $\mathrm{Fe(hfpd)_2Mc^3}$ are consistent with a 6-coordinated, high spin Fe^{II} atom [11].



(E)

TABLE V. Details of Planar Fragments of $[Cu(hfpd)_2]_2$trien-Me_6. Equations of Mean Planes are of the form $pX + qY + rZ = d$, where p, q and r are direction cosines referred to orthogonal crystal axes a, b, c*. Deviations of atoms from the mean planes are given in parentheses.

	p	*q*	*r*	*d*
Plane A	O(2), O(3), N(1), N(2)			r.m.s. deviation 0.034 Å
	0.8390	0.0932	−0.5361	1.5369
	[O(2) 0.035, O(3) −0.034, N(1) −0.034, N(2) 0.033, Cu(1) −0.046, O(1) −2.336, O(4) 2.292, C(11) −1.133, C(12) 1.229, C(13) −0.175, C(14) 0.475, C(15) 1.077, C(16) −1.310]			
Plane B	Cu(1), O(1), O(2)			
	0.5550	−0.5944	0.5820	−0.7310
	[C(1) 0.638, C(2) 0.335, C(3) 0.603, C(4) 0.446, C(5) 0.750]			
Plane C	Cu(1), O(3), O(4)			
	0.1946	0.8050	0.5604	2.6390
	[C(6) 0.569, C(7) 0.385, C(8) 0.642, C(9) 0.491, C(10) 0.912]			
Plane D	Cu(1), N(1), N(2)			
	0.8510	0.1198	−0.5114	1.5874
	[C(11) −1.072, C(12) 1.280, C(13) −0.195, C(14) 0.423, C(15) 1.028, C(16) −1.366]			
Plane E	O(1), O(2), C(2)–C(4)			r.m.s. deviation 0.023 Å
	0.5908	−0.7495	0.2986	−1.6490
	[O(1) 0.022, O(2) −0.025, C(2) −0.022, C(3) −0.008, C(4) 0.033, Cu(1) 0.500, C(1) 0.005, C(5) 0.037]			
Plane F	O(3), O(4), C(7)–C(9)			r.m.s. deviation 0.031 Å
	−0.1424	0.8763	0.4602	1.7404
	[O(3) 0.025, O(4) −0.035, C(7) −0.021, C(8) −0.017, C(9) 0.049, Cu(1) 0.563, C(6) −0.128, C(10) 0.119]			

Selected angles between planes (°)

A–D	2.2	B–C	92.5
B–E	18.7	B–D	84.1
C–F	20.7	C–D	91.4

Torsion angle: N(1)–C(13)–C(14)–N(2) +52.0°

The m.s. indicates a weak axial interaction with at least one $hfpd^-$ as the highest peak observed is attributed to $[Fe(hfpd)Mc]^+$. The air sensitivity of the complexes also suggests loose axial bonding and the availability of an oxidation pathway. In the octahedral complexes formed from diamines no atmospheric oxidation occurs as complete coordinative saturation has been achieved and the pathway removed.

The corresponding copper(II) complexes, $Cu(hfpd)_2Mc^1$, $Cu(hfpd)Mc^2$ and $Cu(hfpd)_2Mc^3$ were prepared as purple crystalline solids. The IR spectra showed a single carbonyl band at 1665 cm^{-1} suggestive of an ionic hfpd anion [17] and the d.r.s. gave a bond *ca.* 18.5 kk indicating a square coplanar copper(II) environment. The m.s. gave a strongest peak at MLB^+ in all cases, indicating some weak axial interaction with the hfpd anion. The structures are probably directly related to that determined for $Cu(hfpd)_2$(asym-dmen) [17].

Tetradentate Metal Schiff Base Complexes as Ligands (TMSB)

Metal complexes of tetradentate Schiff bases such as N,N′-ethylene-bis-(salicylideneimine), (salen), and bis-acetylacetoneethylenediimine, (acen), have been used as ligands [27]. The complexes have available oxygen donor atoms which can further coordinate to give homo- or heterobinuclear complexes. $Fe(hfpd)_2$, $2H_2O$ reacts with Cu^{II}, Ni^{II} and Co^{II} (salen), and with Cu^{II} and Ni^{II}(acen) to give isolable bimetallic species having the general formula MTSB, $M'(hfpd)_2$.

X-ray crystallographic studies on complexes prepared from Cu(salen) and Cu(hfpd)$_2$ [28], Cu(salen) and Mg(hfpd)$_2$ [29], and Cu(salen) and Co(hfpd)$_2$ [30] show that the metal associated with the Schiff base is in a square planar environment and that the metal associated with the (hfpd) is in an octahedral environment. In the absence of metal exchange reactions occurring it is expected that the complexes (salen)M,Fe(hfpd)$_2$, (M = Cu, Ni, Co) and (acen)M, Fe(hfpd)$_2$, (M = Cu, Ni), would be formed.

This is indicated by the m.s. for the mixed FeCu and FeNi species where P^+ is found as the highest peak and both Fe(hfpd)$_2$ and M(salen) are present in the spectra. However in the spectra of Fe(hfpd)$_2$, Co(salen) peaks corresponding to Co(hfpd)$_2$,Fe(hfpd)$_2$, Co(salen) and Fe(salen) are found indicating that metal exchange can occur. The peaks due to Fe(hfpd)$_2$ and Co(hfpd)$_2$ are present in *ca.* 50:50 abundance ratio. The Mössbauer spectra for the FeCu and FeNi complexes are consistent with the presence of high spin octahedral iron(II) but that for the FeCo species has an I.S. of 0.30 mm sec^{-1} and a Q.S. of 0.83 mm sec^{-1}. This is indicative of high-spin iron(III) [31]. If there had been no metal exchange a normal iron(II) spectrum would have been expected but on exchange the iron is in the Schiff base and so four coordinate and susceptible to oxidation. Studies on the Mössbauer spectra of Fe(salen) complexes reveal that unless strictly anaerobic conditions operate oxidation occurs [33]. This is reflected in the values of the I.S. and Q.S. where Fe(salen) has values of 0.98 and 2.50 mm sec^{-1} before oxidation, and 0.39 and 0.82 mm sec^{-1} after oxidation. The synthesis of (hfpd)$_2$Fe, Co(salen) was carried out under N$_2$ and in vacuo and so any oxidation has probably occurred during the accumulation of the Mössbauer data.

The reaction of Fe(hfpd)$_2$,2H$_2$O with salen in the open atmosphere readily gives the mixed ligand complex Fe(hfpd)(salen) [34]. The IR resembles those of the related M^{III}(acac)(salen) complexes (M = Mn, Co) [35, 36]. The X-ray crystal structures of Co^{III}(acac)(salen) [37] and Co^{III}(bzac)(salen) [38] have been reported and show the salen moiety in a highly strained *cis*-β-conformation, the metal environment being octahedral. Iron(III) mixed ligand complexes had previously been prepared by reacting Fe^{II}(salen) with acac, bzac, or salicylaldehyde in the atmosphere. Fe(hfpd)(salen) has a magnetic moment of 5.58 BM, and this taken with the Mössbauer data (IS = 0.43 mm sec^{-1}; QS = 0.26 mm. sec^{-1}) suggests a hig spin, octahedral metal ion. It is therefore proposed that, by analogy, a configuration similar to those for the Co^{III} complexes is adopted in which the salen ligand is highly strained.

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Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Service. Infra-red spectra were recorded in the 4000–600 cm^{-1} region using a Perkin Elmer 297 infra-red spectrometer and using KBr discs. Mass spectra were recorded using Kratos MS 25 and AE1 MS 12 mass spectrometer.

Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-iron(II), dihydrate was prepared from (hfpd)Na, or other alkali metal hexafluoropentane-2,4-dionates, by trans-metallation using iron(II) sulphate heptahydrate. The reaction was carried out in water and the precipitated red-brown solid filtered and dried *in vacuo* over silica gel [6]. The alkali metal hexafluoropentane-2,4-dionates were prepared by the method of Belcher *et al.* [39].

Other starting materials were prepared by standard literature methods; (tmndH)$^+$(hfpd)$^-$ as in ref. [40]; Mc^1 and Mc^2 by the method of Hideg and Lloyd [41]; Mc^3 by the method of Hay *et al.* [42]; Co(salen) by the method of Calvin and Bailes [43] and the remaining metal complexes of tetradentate Schiff bases by the procedures in ref. [44] and [45].

Preparation of Complexes

The following procedures were used:

(1) Nitrogen bidentate ligands (0.01 mol) dissolved in toluene were reacted with Fe(hfpd)$_2$,2H$_2$O (0.01 mol) dissolved in either toluene or ethanol. The reaction mixture was warmed on a steam bath for 10 minutes and allowed to cool. Crystalline solids precipitated out, were filtered and dried *in vacuo* over silica gel.

[Fe(hfpd)$_3$](tmndH) was prepared following the above procedure.

(2) The preparation of Fe(hfpd)$_2$B with dien-Me$_5$, trien-Me$_6$, and the macrocycles Mc^1, Mc^2 and Mc^3 followed the same general procedure. All operations were carried out under N$_2$ and vacuum using Schlenk tubes. Ethanol was degassed and each of the reactants dissolved in the minimum amount of solvent was transferred by filtration to the reaction Schlenk tube. The reaction mixture was shaken for 15 mins. and the solvent evaporated leaving a dark coloured product which was dried *in vacuo* and maintained under N$_2$ until required for physical measurements.

(3) The reaction of metal Schiff base complexes. MTSB (M = Cu, Ni) with Fe(hfpd)$_2$,2H$_2$O was carried out by dissolving both reactants in a minimum amount of dichloromethane in 1:1 ratio. The mixture was stirred and heated at reflux for 3 hours giving the

corresponding Fe(hfpd)$_2$MTSB complex as a dark coloured precipitate on evaporation of the solvent. The product was dried over silica gel *in vacuo*.

(4) Co(salen) (0.01 mol) was reacted with Fe(hfpd)$_2$,2H$_2$O (0.01 mol) in chloromethane under N$_2$ following the above procedure. The solvent was then evaporated under a stream of N$_2$ and the red solid recovered by filtration and dried *in vacuo*.

(5) Fe(hfpd)(salen),H$_2$O was produced by aerial oxidation of Fe(hfpd)$_2$,2H$_2$O on reaction with H$_2$ salen in chloromethane using a 1:1 molar ratio. The solution was stirred and heated at reflux for 3 hours. The complex precipitated on evaporation of the solvent, was filtered and dried over silica gel *in vacuo*.

Crystal Data

[Cu(hfpd)$_2$]$_2$(trien-M$_6$); $C_{32}H_{34}Cu_2F_{24}N_4O_8$; M = 1185.67; crystallises from toluene as green, hexagonal plates which were extensively twinned by C_6 rotations about the *b*-axis- the normal to the plate. A very small, untwinned crystal was used for data collection; crystal dimensions 0.18 × 0.04 × 0.18 mm. Monoclinic, $a = 10.268(3)$, $b = 25.255(8)$, $c = 10.392(3)$ Å, $\beta = 119.29(2)°$, $U = 2350.3(12)$ Å^3, $D_m = 1.72$, $D_c = 1.675$ g cm^{-3}, $Z = 2$; space group $P2_1/a$ (a non-standard setting of $P2_1/c$, C_{2h}^5, No. 14), Mo K$_\alpha$ radiation ($\bar{\lambda} = 0.71069$ Å), μ(Mo K$_\alpha$) = 10.46 cm^{-1}, $F(000) = 1184$.

Three-dimensional X-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3m diffractometer by the omega-scan method. 1261 independent reflections for wich $I/\sigma(I) > 2.0$ were corrected for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were detected and placed in calculated positions (C–H 0.96 Å, N–C–H (methyl) 111°); their contributions were included in structure factor calculations (B = 12.0 Å^2) but no refinement of positional parameters was permitted. The geometries of each of the four trifluoromethyl groups was constrained (C–F 1.315 Å, F–C–F 107.8°) during the latter stages of refinement which converged at R 0.1213 with allowance for anisotropic thermal motion of copper, fluorine and oxygen and for the anomalous scattering of copper. Table VI lists the atomic positional parameters with estimated standard deviations. Tables of thermal vibrational parameters with estimated standard deviations, predicted hydrogen atom positional parameters and observed structure amplitudes and calculated structure factors are available from the authors.

Scattering factors were taken from ref. [46]; unit weights were used throughout the refinement; computer programs formed part of the Sheffield X-ray system.

TABLE VI. Atomic Positional Parameters with Estimated Standard deviations for [Cu(hfpd)$_2$]$_2$trien-Me$_6$.[a]

	X/a	*Y/b*	*Z/c*
Cu(1)	0.1584(4)	0.11125(15)	0.0149(4)
F(1)	−0.051(1)	0.1123(10)	0.357(2)
F(2)	0.138(2)	0.0618(6)	0.463(2)
F(3)	0.150(2)	0.1411(8)	0.537(2)
F(4)	0.564(3)	0.2029(12)	0.334(4)
F(5)	0.411(4)	0.2670(9)	0.257(3)
F(6)	0.486(4)	0.2359(12)	0.472(2)
F(7)	0.505(3)	−0.0115(8)	0.332(3)
F(8)	0.558(3)	0.0628(10)	0.442(2)
F(9)	0.697(2)	0.0311(11)	0.361(3)
F(10)	0.629(3)	0.1020(10)	−0.091(3)
F(11)	0.626(3)	0.1768(11)	0.001(3)
F(12)	0.459(3)	0.1581(13)	−0.218(2)
O(1)	0.0730(18)	0.1065(9)	0.1840(19)
O(2)	0.2740(23)	0.1742(8)	0.1314(22)
O(3)	0.3238(21)	0.0662(9)	0.1581(21)
O(4)	0.3090(19)	0.1190(10)	−0.0972(20)
N(1)	−0.009(3)	0.1595(9)	−0.132(2)
N(2)	0.042(2)	0.0478(8)	−0.120(2)
C(1)	0.095(1)	0.1107(6)	0.419(1)
C(2)	0.141(3)	0.1289(9)	0.299(3)
C(3)	0.260(3)	0.1654(13)	0.355(3)
C(4)	0.321(4)	0.1842(14)	0.265(4)
C(5)	0.447(2)	0.2232(7)	0.335(2)
C(6)	0.558(2)	0.0361(7)	0.332(2)
C(7)	0.455(3)	0.0666(11)	0.186(3)
C(8)	0.522(4)	0.0876(13)	0.112(4)
C(9)	0.442(3)	0.1150(13)	−0.023(3)
C(10)	0.541(2)	0.1385(8)	−0.085(2)
C(11)	−0.075(4)	0.1948(16)	−0.065(4)
C(12)	0.044(4)	0.1944(14)	−0.211(4)
C(13)	−0.121(3)	0.1237(13)	−0.231(3)
C(14)	−0.064(3)	0.0736(13)	−0.262(3)
C(15)	0.143(4)	0.0122(13)	−0.148(4)
C(16)	−0.048(3)	0.0170(12)	−0.066(3)

[a] The estimated standard deviations of the atoms of the trifluoromethyl groups were derived from the e.s.ds. of the group parameters which were used to refine them.

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