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Bis(1,2-diaminobenzene-*N*)bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-*O*,*O*′)iron(II), -cobalt(II) and -nickel(II) at low temperature[1]

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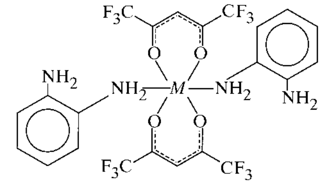
Addition of 1,2-phenylenediamine to solutions of bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-*O*,*O*′)cobalt(II), -iron(II) and -nickel(II) resulted in crystals containing centrosymmetric octahedral complexes with two amines per metal atom. In all three isostructural complexes, *i.e.* $[M(C_5HF_6O_2)_2(C_6H_8N_2)_2]$ where M = Fe, Cu and Ni, the two C—N bonds differ significantly in length by an average of 0.031 (3) Å. The phenyl C—C bonds display a pattern of small differences, the C—C bond between the amines being longer than the shortest phenyl C—C bonds by an average of 0.022 (4) Å.

Comment

The title complexes were synthesized in order to explore the coordination of bidentate ligands with M(hfac)$_2$ complexes (hfac is 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-*O*,*O*′). Tetramethylethylenediamine and other strong bidentate bases have been observed to coordinate to Fe(hfac)$_2$ in a bidentate fashion to form neutral monomers (Dickman, 1998; Bailey *et al.*, 1981). In contrast, addition of a bidentate nitrone to Fe(hfac)$_2$ resulted in ligand exchange to produce a complex salt (Villamena *et al.*, 1998). The reason for this difference is not clear. 1,2-Phenylenediamine (opda) was chosen for the present study because it is a weaker σ donor than tetramethylethylenediamine. Even when opda was added in a 1:1 ratio to Co(hfac)$_2$, Fe(hfac)$_2$ and Ni(hfac)$_2$ hydrates, only 2:1 amine–metal complexes were isolated from CHCl$_3$/*n*-heptane solution. The resulting crystal structures show discrete centrosymmetric octahedrally coordinated complexes, with two mondentate opda ligands per metal atom (Fig. 1). The two amine functions on each phenyl ring have different C—N bond lengths. The bond to the metal-coordinated amine, C1—N1, is longer than C2—N2 by 0.031 (3) Å on average. Shortening of the non-coordinated amine function has been seen previously in a monodentate opda complex of bis(1,3-diphenyl-1,3-propanedionato-*O*,*O*′)nickel(II) [difference of 0.027 (3) Å; Hotz *et al.*, 1987] and in [Cr(opda)$_2$(NCS)$_2$] [difference of 0.059 (3) Å; Jubb *et al.*, 1991]. However, in [Ni(opda)$_4$]$^{2-}$ (Elder *et al.*, 1974) and in a macrocyclic Cd complex (Nelson *et al.*, 1982), monodentate opda showed no significant difference in the C—N bond lengths. Both of these structures had either poor data (*e.g.* twinning) or larger than usual s.u.'s.


(I) M = Fe
(II) M = Co
(III) M = Ni

In the present structures, bis(1,2-diaminobenzene-*N*)-bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-*O*,*O*′)iron(II), (I), bis(1,2-diaminobenzene-*N*)bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-*O*,*O*′)cobalt(II), (II), and bis(1,2-diaminobenzene-*N*)bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-*O*,*O*′)nickel(II), (III), the N2 NH$_2$ group is slightly more planar than that of N1, as evidenced by the out-of-plane distances of the C atoms bound to the N atoms from the planes of the amines. This value averages 1.07 (4) Å for C2 out of the H1N2—N2—H2N2 plane compared with 1.25 (3) Å for C1 out of the H1N1—N1—H2N1 plane.

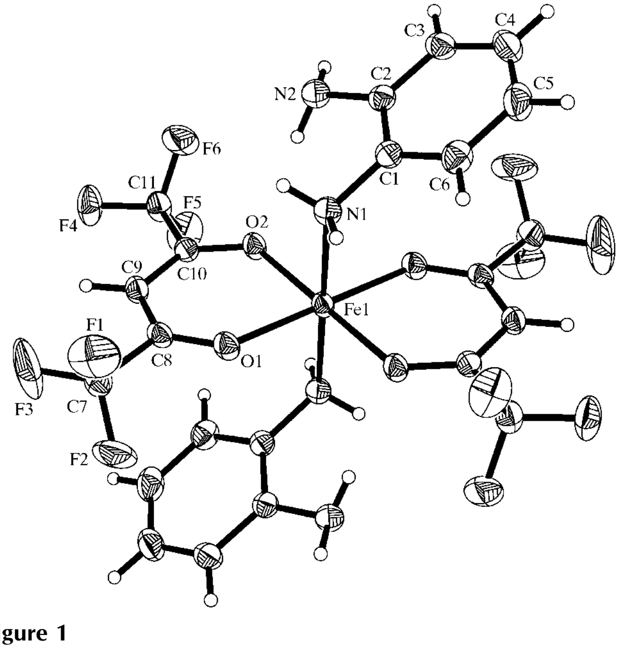


Figure 1
Displacement ellipsoid plot (50% probability) of compound (I) showing the atom-numbering scheme. H atoms are drawn as small circles of arbitrary radii.

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[1] Dedicated to the memory of Dr Leigh C. Porter (1955–1999).

The phenyl C—C bond lengths show a pattern of differences not seen in previous structures. The C1—C2 bond, averaging 1.405 (3) Å, is longer by 0.022 (4) Å than the C4—C5 and C5—C6 bonds, which average 1.383 (4) Å. The C2—C3, C5—C6 and C6—C1 bond lengths fall between these values, with an average of 1.393 (4) Å.

A network of apparent intermolecular hydrogen bonds involving H atoms on N1 as donors to N2 and F3 extends through the crystal and an intramolecular hydrogen bond between N2 and O2 is also observed. This intramolecular hydrogen bond, although not especially short, might be one reason that only 2:1 complexes were isolated.

Experimental

Crystals were grown by addition of stoichiometric amounts of opda to $CHCl_3$ solutions of the appropriate hydrated M(hfac)$_2$ complexes (Morris *et al.*, 1968) with stirring and gentle heating, followed by addition of *n*-heptane and slow evaporation at room temperature in loosely covered beakers. ^{19}F NMR spectra were measured on a Varian Mercury 300 MHz spectrometer interfaced with a Sun Microsystems workstation. Spectra were recorded at 294.5 K with CF_3COOH in $CDCl_3$ as an external reference. No peak was observed for (I), and peaks for (II) and (III) were observed at 60.79 and 48.40 p.p.m. in $CDCl_3$, respectively. IR spectra were recorded on a Nicolet FT-7000 spectrometer as KBr pellets. The IR spectra were essentially identical for all three compounds, with peaks at (cm^{-1}): 1637 (*s*), 1600 (*m*), 1558 (*m*), 1531 (*m*), 1506 (*m*), 1481 (*s*), 1350 (*w*), 1261 (*s*), 1216 (*s*), 1195 (*m*), 1151 (*s*), 1134 (*s*), 1097 (*w*), 1074 (*m*), 1060 (*m*), 931 (*w*), 864 (*w*), 856 (*w*), 800 (*s*), 777 (*w*), 756 (*m*), 723 (*w*), 670 (*m*), 589 (*m*), 524 (*w*), 468 (*m*). Some splitting of peaks was evident in the case of (I), presumably due to oxidation in the pellet press.

Compound (I)

Crystal data

$[Fe(C_5HF_6O_2)_2(C_6H_8N_2)_2]$
$M_r = 686.25$
Monoclinic, $P2_1/n$
$a = 7.8148\ (1)$ Å
$b = 10.9332\ (2)$ Å
$c = 15.4893\ (3)$ Å
$\beta = 99.002\ (1)^\circ$
$V = 1307.12\ (4)$ Å^3
$Z = 2$

$D_x = 1.744$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.29$–28.24°
$\mu = 0.701$ mm^{-1}
$T = 173\ (2)$ K
Prism, red
0.40 × 0.37 × 0.16 mm

Data collection

Bruker SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.620, T_{\max} = 0.735$
13 875 measured reflections

3129 independent reflections
2818 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 28.24^\circ$
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.107$
$S = 1.002$
3129 reflections
233 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 1.4920P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.06$ e Å^{-3}
$\Delta\rho_{\min} = -0.80$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0150 (16)

Table 1
Selected geometric parameters (Å, °) for (I).

Fe1—O2	2.0468 (13)	C1—C2	1.407 (3)
Fe1—O1	2.0593 (13)	C2—C3	1.397 (3)
Fe1—N1	2.2803 (17)	C3—C4	1.387 (3)
N1—C1	1.443 (2)	C4—C5	1.378 (4)
N2—C2	1.415 (3)	C5—C6	1.398 (3)
C1—C6	1.390 (3)		
O2—Fe1—O1	86.59 (5)	O1^{i}—Fe1—N1	92.12 (6)
O2^{i}—Fe1—O1	93.41 (5)	O1—Fe1—N1	87.88 (6)
O2—Fe1—N1	93.04 (6)	C1—N1—Fe1	119.06 (12)
O2^{i}—Fe1—N1	86.96 (6)		

Symmetry code: (i) $-x, -y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N1$\cdots$N2^{i}	0.88 (3)	2.30 (3)	3.137 (3)	158 (2)
N1—H2N1$\cdots$F3^{ii}	0.87 (3)	2.59 (3)	3.382 (2)	151 (2)
N2—H2N2$\cdots$O2	0.86 (3)	2.26 (3)	3.125 (2)	177 (2)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Compound (II)

Crystal data

$[Co(C_5HF_6O_2)_2(C_6H_8N_2)_2]$
$M_r = 689.33$
Monoclinic, $P2_1/n$
$a = 7.769$ Å
$b = 10.9013\ (1)$ Å
$c = 15.4431\ (1)$ Å
$\beta = 99.288\ (1)^\circ$
$V = 1290.729\ (14)$ Å^3
$Z = 2$

$D_x = 1.774$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6146 reflections
$\theta = 2.30$–28.56°
$\mu = 0.790$ mm^{-1}
$T = 158\ (2)$ K
Block, orange
0.36 × 0.32 × 0.30 mm

Table 3
Selected geometric parameters (Å, °) for (II).

Co1—O2	2.0433 (11)	C1—C2	1.405 (2)
Co1—O1	2.0562 (11)	C2—C3	1.395 (2)
Co1—N1	2.2243 (13)	C3—C4	1.385 (3)
N1—C1	1.4426 (19)	C4—C5	1.386 (3)
N2—C2	1.415 (2)	C5—C6	1.394 (3)
C1—C6	1.388 (2)		
O2—Co1—O1	88.55 (4)	O1—Co1—N1	87.72 (5)
O2^{i}—Co1—O1	91.45 (4)	O1^{i}—Co1—N1	92.28 (5)
O2—Co1—N1	92.66 (5)	C1—N1—Co1	120.13 (9)
O2^{i}—Co1—N1	87.34 (5)		

Symmetry code: (i) $-x, -y, -z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N1$\cdots$N2^{i}	0.86 (3)	2.33 (3)	3.142 (2)	159 (2)
N1—H2N1$\cdots$F3^{ii}	0.94 (3)	2.54 (3)	3.388 (2)	151 (2)
N2—H2N2$\cdots$O2	0.88 (3)	2.21 (3)	3.087 (2)	176 (2)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Data collection

Bruker SMART area-detector diffractometer
ω scans
20 859 measured reflections
5646 independent reflections
4392 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.037$
$\theta_{\rm max} = 35.52^\circ$
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 17$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.137$
$S = 1.005$
5646 reflections
233 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0766P)^2 + 0.7210P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\rm max} = 1.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.00$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.018 (2)

Compound (III)

Crystal data

$[\mathrm{Ni(C_5HF_6O_2)_2(C_6H_8N_2)_2}]$
$M_r = 689.11$
Monoclinic, $P2_1/n$
$a = 7.7597$ (1) Å
$b = 10.9286$ (1) Å
$c = 15.3948$ (3) Å
$\beta = 98.813$ (1)°
$V = 1290.11$ (3) Å^3
$Z = 2$

$D_x = 1.774$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5479 reflections
$\theta = 2.29$–28.26°
$\mu = 0.878$ mm^{-1}
$T = 173$ (2) K
Block, green
0.46 × 0.40 × 0.35 mm

Data collection

Bruker SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\rm min} = 0.672, T_{\rm max} = 0.797$
13 585 measured reflections

3079 independent reflections
2784 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 28.26^\circ$
$h = -10 \rightarrow 9$
$k = -13 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.112$
$S = 1.011$
3079 reflections
232 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 1.58P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\rm max} = 1.10$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.72$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III).

Ni1—O2	2.0225 (15)	C1—C2	1.404 (3)
Ni1—O1	2.0311 (14)	C2—C3	1.395 (3)
Ni1—N1	2.164 (2)	C3—C4	1.384 (4)
N1—C1	1.448 (3)	C4—C5	1.380 (4)
N2—C2	1.411 (3)	C5—C6	1.390 (4)
C1—C6	1.389 (3)		
O2—Ni1—O1	90.12 (6)	O1$^{\rm i}$—Ni1—N1	92.97 (7)
O2$^{\rm i}$—Ni1—O1	89.88 (6)	O1—Ni1—N1	87.03 (7)
O2—Ni1—N1	92.75 (7)	C1—N1—Ni1	119.91 (14)
O2$^{\rm i}$—Ni1—N1	87.25 (7)		

Symmetry code: (i) $-x, -y, -z$.

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···N2$^{\rm i}$	0.84 (3)	2.38 (3)	3.175 (3)	156 (3)
N1—H2N1···F3$^{\rm ii}$	0.88 (3)	2.61 (3)	3.435 (3)	156 (2)
N2—H2N2···O2	0.90 (3)	2.18 (3)	3.083 (3)	177 (3)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

For each crystal, decay was monitored by recollection of the first 50 frames at the end of the data collection. H atoms were refined isotropically in observed positions. For all three complexes, final C—H distances ranged from 0.91 (3) to 0.99 (4) Å and final N—H distances ranged from 0.84 (3) to 0.94 (3) Å. In compound (I), the highest peak in the final difference Fourier map was 1.14 Å from F3, for compound (II) it was 1.09 Å from F3, and for compound (III) it was 1.11 Å from F3.

For all compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1091). Services for accessing these data are described at the back of the journal.

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