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Bis[tris(1-methyl-1*H*-imidazol-2-yl)phosphine-κ^3N^3]iron(II) tetrachloroferrate(II) methanol tetrasolvate (*ca* 153 K) and bis[tris(1-methyl-1*H*-imidazol-2-yl)methanol-κ^3N^3]iron(III) bis[tetrachloroferrate(III)] chloride (redetermination, *ca* 153 K)

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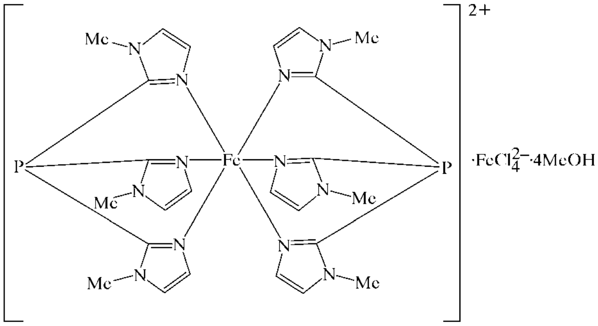
The first of the title compounds, [Fe(C$_{12}$H$_{15}$N$_6$P)$_2$][FeCl$_4$]·4CH$_4$O, is the first homoleptic bis(ligand)iron(II) species reported for this phosphorus bridgehead ligand; interestingly, the complex is isomorphous with its tris(1-methyl-1*H*-imidazol-2-yl)methanol counterpart, the second of the title compounds, [Fe(C$_{13}$H$_{16}$N$_6$O)$_2$][FeCl$_4$]$_2$Cl. In both compounds, the Fe atom of the cation lies on an inversion centre. The structure determinations presented here allow an interesting comparison of iron(II) and iron(III) species in similar coordination environments.

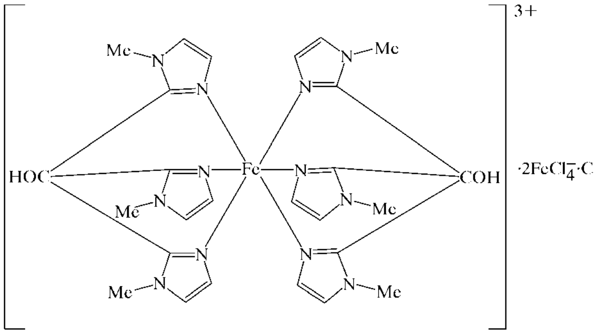
Comment

The chemistry of metal complexes of tris(pyrazolyl)-type ligands has been extensively explored in a number of dimensions, homoleptic bis(ligand) complexes, in which the ligand functions as a symmetrical tripod about a six-coordinate metal atom, being of particular interest to us, particularly in respect of the spin-crossover behaviour exhibited by iron-containing species (Anderson *et al.*, 2000; Reger *et al.*, 2000). By contrast, tris(imidazolyl)-type ligands are much less extensively studied and it was our objective to prepare and study homoleptic bis(ligand) complexes of this type with iron for comparative purposes. At the time this work was undertaken, there were no structurally characterized species of this type; a number of complexes were prepared and some initial structural studies were undertaken as a preliminary to further work, which was forestalled by the appearance of similar work in the field (Wu *et al.*, 1999). Nevertheless, at the structural level, local achievements represent independent results of some significance and interest, and we report them here.

The only homoleptic bis[tris(imidazolyl)ligand]iron(III) species previously structurally defined are the second title compound, [Fe{(mim)$_3$COH}$_2$][FeCl$_4$]$_2$Cl (mim is 1-methyl-1*H*-imidazol-2-yl), (II), previously recorded in a room-temperature study (Wu *et al.*, 1999), and the complex [Fe*L*$_2$](ClO$_4$)$_3$ [*L* = (mim)$_2$(4-CMe$_2$Pr^{i}im)COMe], in which the ligand does not have threefold symmetry (Chauvin *et al.*, 2003). Our parallel low-temperature study of (II), recorded here, is of superior precision, enabling meaningful location of H atoms, including that of the methanol hydroxy H atom of the (mim)$_3$COH ligand, the location of which is at variance with that of the room-temperature study wherein atoms were located from difference maps but not refined. Presented as a connected set, our model is otherwise essentially in agreement with the previous study; one-half of the formula unit, with the Fe and Cl atoms residing on crystallographic inversion centres, comprises the asymmetric unit of the structure. The cation is depicted in Fig. 1, and geometric parameters are presented in Table 2. The methanol H atom is hydrogen bonded to the free chloride ion [H0···Cl5(x, y, $1 + z$) = 2.49 Å], the nearest neighbours of the latter being an inversion-related pair.



(I)



(II)

Tris(heterocycle)tripod-type ligands with phosphorus as the bridgehead are less well studied than those where the bridgehead is a first-row atom, and we had considered it of significance to examine the possible influence of a second-row atom, itself potentially a 'soft' donor, in this role. A diversity of structurally characterized complexes have been defined for a variety of divalent metal ions, none of these being of the homoleptic bis(ligand) six-coordinate metal form; with iron, a binuclear iron(III) species has been defined, wherein one such

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ligand binds as a tripod to each six-coordinate metal (Wu *et al.*, 1990). Title compound (I) is isomorphous with its (mim)$_3$COH ligand counterpart (Wu *et al.*, 1999). In (I) (Fig. 2 and Table 1), one-half of the formula unit comprises the asymmetric unit of the structure, with the Fe atom of the complex cation again on a crystallographic inversion centre, while that of the anion is on a crystallographic 2-axis. Again, the precision of the low-temperature determination permits meaningful location of all H atoms. Both of the solvent hydroxy H atoms are hydrogen bonded to the same Cl atom of the anion [Cl2···H01(x, $1 - y$, $\frac{1}{2} + z$) = 2.22 Å and Cl2···H02($x - \frac{1}{2}$, $\frac{1}{2} - y$, $-z$) = 2.25 Å] at unusually short distances and consequently the associated Fe—Cl distance is considerably elongated compared with its non-hydrogen-bonded counterpart [Fe2—Cl1/Cl2 = 2.2797 (5) and 2.3648 (7) Å].

The two arrays (I) and (II) permit interesting comparisons between parallel arrays of iron(II) and iron(III). In the tetrahaloferrate anions, the Fe—Cl distances in (II), which lie within a narrow range [mean 2.202 (8) Å], are appreciably shorter than the more divergent values found in (II), in keeping with the change in electron configuration. The angular geometry within the d^5 species is similarly closely tetrahedral [range 107.97 (2)–110.51 (2)°], whereas within the more distorted d^6 array, the angle between the pair of short Fe—Cl1 distances is increased (as might be expected) to 120.50 (3)°; the Fe—Cl distances, more generally, for the two species are in agreement with those defined in many similar arrays.

Within the cations, the Fe—N distances lie within a narrow range in both compounds [mean 1.979 (5) Å for (I) and 1.951 (4) Å for (II)], in keeping with low-spin electron distributions for d^5 and d^6 configurations in (II) and (I), respectively; angular geometries within the tripod are reasonably regular in each case, but it is interesting to observe the substantial increase in the N—Fe—N angle [mean 86.6 (9)° for (II) and 89.9 (16)° for (I)], concomitant with a minor increase in the Fe—N distance and perhaps contingent upon the substantial increase in size of the bridgehead atom on passing from C to P [mean C—C = 1.530 (6) Å and C—P = 1.817 (1) Å]. In the previously recorded counterpart of (I), *viz.* with the COH bridgehead, the mean Fe—N distance (at 295 K) is 1.973 (12) Å but the mean N—Fe—N angle is reduced to 86.5 (8)°. Deviations of the Fe atom from the C$_3$N$_2$ heterocycle planes are minimal in (I) [0.010 (3), 0.055 (3) and 0.009 (3) Å] but much more substantial in (II) [0.226 (2), 0.256 (3) and 0.047 (3) Å], suggestive of some strain in the latter system.

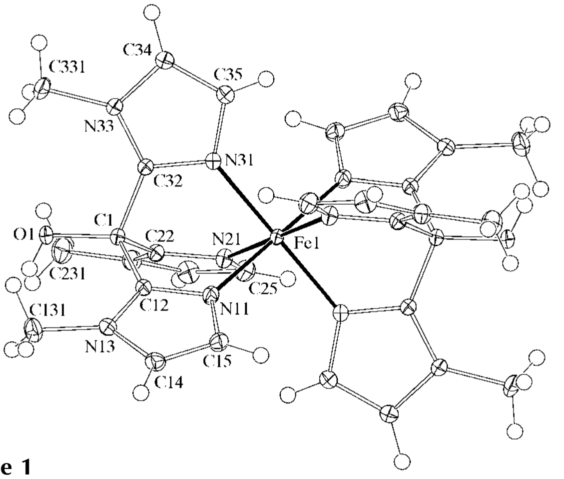

Figure 1
A projection of the cation of (II). Displacement ellipsoids at the 50% probability level are shown for the non-H atoms, with the H atoms having arbitrary radii of 0.1 Å.

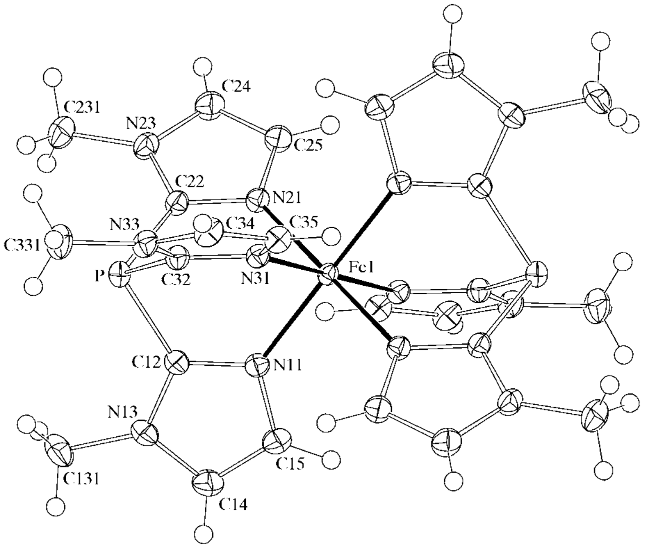

Figure 2
A projection of the cation of (I). Displacement ellipsoids at the 50% probability level are shown for the non-H atoms, with the H atoms having arbitrary radii of 0.1 Å.

Assuming it is more likely that any impact on ligand geometries will arise from the change in bridgehead rather than the metal atom electron configuration, it is of interest to compare these factors between the two systems. In (II), at the bridgehead, the mean C—C—C angle is 105.5 (13)°, while in (I), the mean C—P—C angle is 95.13 (13)°; the former is diminished from the tetrahedral angle and the latter is augmented from the orthogonality of pure π bonding. There is little impact on the ring distances, the only significant changes being to either side of atom N3 [mean N3—C2 = 1.355 (3) and 1.345 (3) Å, and mean N3—C4 = 1.369 (4) and 1.382 (4) Å for (I) and (II), respectively]. Changes in the angles are more pronounced, most notably so exocyclically and, unsurprisingly, at atoms Nn1 [mean Fe—Nn1—Cn2 = 124.0 (5) and 121.5 (10)°, and mean Fe—Nn1—Cn5 = 129.9 (9) and 130.9 (6)° for (I) and (II), respectively] and Cn2 [mean X—Cn2—Nn1 = 123.7 (4) and 119.1 (19)°, and mean X—Cn2—Nn3 = 125.7 (5) and 130.5 (12)° for (I) (X = P) and (II) (X = C), respectively], with surprisingly large differences exocyclically at atom N3 [mean Cn31—Nn3—C2 = 126.7 (7) and 129.8 (3)°, and mean Cn31—Nn3—C4 = 125.9 (3) and 122.9 (2)° for (I) and (II), respectively].

Experimental

Complex (I) was obtained on addition of a solution of P(mim)$_3$ (0.047 g, 0.19 mmol) in methanol (3.5 ml) to a stirred solution of

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iron(II) chloride (0.024 g, 0.19 mmol) in methanol (3 ml). The yellow–brown solution rapidly became blood red. Diethyl ether vapour was allowed to diffuse into the solution. After 2 d, the orange–red crystals that had formed were collected, washed with diethyl ether (3 × 1.5 ml) and dried in a stream of nitrogen to give the product (0.077 g, 89%). The preparation of (II) has been described elsewhere (Wu *et al.*, 1999).

Compound (I)

Crystal data

$[Fe(C_{12}H_{15}N_6P)_2][FeCl_4]\cdot 4CH_4O$
$M_r = 930.21$
Orthorhombic, *Pbcn*
$a = 16.9011\ (10)$ Å
$b = 12.9824\ (8)$ Å
$c = 18.3248\ (11)$ Å
$V = 4020.8\ (4)$ Å^3
$Z = 4$
$D_x = 1.537$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 6152 reflections
$\theta = 2.6$–$37.2°$
$\mu = 1.12$ mm^{-1}
$T = 150\ (2)$ K
Prism, red
0.20 × 0.20 × 0.15 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.69$, $T_{max} = 0.83$
82 795 measured reflections

10 596 independent reflections
6611 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 37.5°$
$h = -28 \rightarrow 28$
$k = -22 \rightarrow 22$
$l = -31 \rightarrow 31$

Refinement

Refinement on F
$R = 0.04$
$wR = 0.042$
$S = 0.98$
6611 reflections
237 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0003F^2]$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.96$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

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

Fe1—N11	1.9851 (13)	Fe1—N31	1.9792 (12)
Fe1—N21	1.9755 (13)		
N11—Fe1—N21	89.01 (5)	N21—Fe1—N31	88.28 (5)
N11—Fe1—N31	88.99 (5)		

Compound (II)

Crystal data

$[Fe(C_{13}H_{16}N_6O)_2][FeCl_4]_2Cl$
$M_r = 1031.24$
Monoclinic, $P2_1/c$
$a = 9.7792\ (9)$ Å
$b = 14.8534\ (10)$ Å
$c = 13.3529\ (17)$ Å
$\beta = 93.835\ (2)°$
$V = 1935.2\ (3)$ Å^3
$Z = 2$

$D_x = 1.77$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7062 reflections
$\theta = 2.4$–$26.8°$
$\mu = 1.78$ mm^{-1}
$T = 150\ (2)$ K
Cuboid, dark red
0.45 × 0.45 × 0.40 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.68$, $T_{max} = 0.80$
38 960 measured reflections

10 066 independent reflections
7754 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 37.7°$
$h = -16 \rightarrow 16$
$k = -25 \rightarrow 25$
$l = -22 \rightarrow 22$

Refinement

Refinement on F
$R = 0.037$
$wR = 0.067$
$S = 1.02$
7754 reflections
238 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.003F^2]$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 1.44$ e Å^{-3}
$\Delta\rho_{min} = -0.78$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

Fe1—N11	1.9500 (13)	Fe1—N31	1.9468 (13)
Fe1—N21	1.9547 (14)		
N11—Fe1—N21	85.59 (6)	N21—Fe1—N31	87.13 (6)
N11—Fe1—N31	87.12 (5)		

H atoms were located from difference Fourier maps and then placed at idealized positions [C—H = 0.95 Å, and $U_{iso}(H) = 1.25U_{eq}(C_{CH})$ and $1.5U_{eq}(C_{CH_3})$] and not refined.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *Xtal*3.5 (Hall *et al.*, 1995); program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5; molecular graphics: *Xtal*3.5; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1445). Services for accessing these data are described at the back of the journal.

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