Structure of Hexakis(N-methylimidazole-N')iron(II) Tetraphenylborate Dichloromethane Solvate

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Abstract. $[Fe(C_4H_6N_2)_6][B(C_6H_5)_4]_2.CH_2Cl_2$, $M_r =$ 1271·88, monoclinic, $P2_1/c$, $a = 20·5320$ (6), $b =$ 15·113 (3), $c = 23·611$ (7) Å, $\beta = 109·01$ (3)°, $V =$ 6926·9 (1) Å^3, $Z = 4$, $D_x = 1·23$ g cm^{-3}, μ(Mo $K\alpha$) = 0·70966 Å, graphite monochromator, $\mu = 3·37$ cm^{-1}, $F(000) = 2680$, $T = 298$ K, $R = 0·057$ for 2310 unique observed reflections. The asymmetric unit consists of a single $[Fe(C_4H_6N_2)_6]^{2+}$ cation, two distinct BPh_4^- anions, and one CH_2Cl_2. The Fe atom is octahedrally coordinated by six N-methylimidazole ligands. The six Fe—N bond distances per cation range from 2·174 (11) to 2·228 (10) Å, the average being 2·207 (12) Å. This average distance is within the range previously observed for high-spin ferrous complexes. The ring planes of N-methylimidazole ligands that lie *trans* to each other have interplane angles of 17·56, 18·48 and 157·56°. These ring planes lie approximately either parallel or perpendicular to equatorial Fe—N bonds.

Experimental. All procedures for preparation of the compound were performed under an Ar atmosphere. A tenfold molar excess of N-methylimidazole was added to a solution of anhydrous $FeCl_3$ in absolute ethanol. After refluxing for 1 h a twofold molar excess over Fe of NaBPh$_4$ was added to the cooled solution, resulting in the formation of a yellowish-red solid, which was washed and vacuum dried. This solid was dissolved in THF containing excess N-methylimidazole and reduced by dropwise addition of $(Me_2Si)_2S$, which resulted in the formation of a white crystalline solid. This solid was recrystallized from dichloromethane–hexanes to give analytically pure $[Fe(C_4H_6N_2)_6](BPh_4)_2.CH_2Cl_2$. The identical compound has since been prepared by reaction of $FeCl_2.4H_2O$ and excess N-methylimidazole in ethanol followed by metathesis with NaBPh$_4$ and recrystallization (Wu & Kurtz Jr, unpublished results). A colorless single crystal of approximate dimensions 0·10 × 0·12 × 0·15 mm was mounted in a Lindemann-glass capillary under Ar. Monoclinic symmetry was indicated by the automatic indexing routine *ALICE*

(Jacobson, 1976) and subsequently verified by X-ray photographs; the space group was uniquely determined to be $P2_1/c$ *via* the extinctions $h0l$: $l \neq 2n$ and $0k0$: $k \neq 2n$. Accurate lattice parameters were obtained by least-squares refinement of 14 high-angle reflections. Intensity data (5859 reflections) were collected at 298 K using an ω-scan technique over the hkl and $hk\bar{l}$ octants on a Datex four-circle diffractometer to a 2θ maximum of 41°, $(\sin\theta)/\lambda = 0·49$ Å^{-1} (limited due to the poorly diffracting nature of the crystal). Three standards were monitored periodically and showed no significant decomposition over the course of data collection. The data were corrected for Lorentz–polarization and for absorption using *ABSN* (Karcher, 1981) (the transmittance ranged from 0·73 to 0·99); 2626 reflections were considered observed with $I \geq 1·25\sigma(I)$. The estimated error in each intensity was calculated by $\sigma(I_o)^2 = C_t + KC_b + (0·03C_t)^2 + (0·03C_b)^2$, where K is a counting time factor, C_t and C_b are the total and background counts respectively, and the factor 0·03 represents an estimate of the non-statistical errors. Equivalent reflections were averaged yielding 2310 unique observed reflections. The internal agreement factor $R_{int} = 0·029$. The positions of the Fe atom and several lighter atoms were determined by our automated superposition analysis routine *ALCAMPS* (Richardson, Kim & Jacobson, 1986) using Harker vectors selected from a standard sharpened Patterson map. Atomic scattering factors were taken from Cromer & Waber (1974); H scattering factors were taken from Stewart, Davidson & Simpson (1965); real and imaginary corrections for anomalous dispersion of the Fe and Cl atoms were obtained from Cromer & Liberman (1974). Structure-factor calculations and refinements, using a block-matrix least-squares procedure, were performed using the program *ALLS* (Lapp & Jacobson, 1979); electron-density-map calculations used *FOUR* (Powell & Jacobson, 1980). After all non-H atoms had been located, full-matrix least-squares refinement was carried out using *ALLS*. The H positions were calculated and updated in the later stages of refinement (but not refined). Six H atoms with half occupancy were used for the methyl H atoms to simulate free rotation about the bond axis. The function

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Table 1. Atomic coordinates ($\times 10^4$) and average isotropic thermal parameters ($\text{Å}^2 \times 10^3$)

$U_{av} = \frac{1}{3}\sum_i\sum_j U_{ij}\mathbf{a}_i \cdot \mathbf{a}_j a_i^* a_j^*$ where the temperature factors are defined as $\exp(-2\pi^2\sum_i\sum_j U_{ij}h_ih_j a_i^* a_j^*)$.

|	x	y	z	U_{av}
Fe1	2661 (1)	267 (1)	325 (8)	85
B1	1498 (11)	4069 (10)	−1943 (8)	76
C11	1149 (10)	4895 (9)	−2438 (6)	77
C12	1547 (7)	5313 (12)	−2755 (8)	89
C13	1257 (11)	5953 (12)	−3206 (8)	105
C14	577 (13)	6189 (10)	−3342 (7)	115
C15	173 (7)	5763 (13)	−3073 (8)	88
C16	461 (10)	5128 (11)	−2630 (7)	85
C21	1121 (6)	3999 (13)	−1408 (5)	79
C22	928 (7)	4787 (13)	−1200 (7)	99
C23	690 (8)	4799 (12)	−713 (8)	114
C24	627 (8)	4015 (18)	−435 (7)	112
C25	794 (8)	3225 (13)	−645 (8)	120
C26	1071 (7)	3211 (10)	−1105 (8)	95
C31	1335 (9)	3201 (10)	−2393 (6)	82
C32	764 (8)	2648 (13)	−2510 (6)	89
C33	632 (9)	1925 (10)	−2918 (8)	98
C34	1067 (11)	1758 (11)	−3244 (7)	104
C35	1650 (10)	2283 (13)	−3137 (7)	96
C36	1792 (7)	2993 (10)	−2727 (7)	70
C41	2323 (9)	4207 (16)	−1609 (5)	77
C42	2575 (11)	5053 (14)	−1380 (7)	86
C43	3265 (14)	5240 (12)	−1050 (8)	106
C44	3717 (11)	4552 (17)	−923 (8)	118
C45	3520 (11)	3725 (17)	−1125 (7)	111
C46	2838 (13)	3548 (9)	−1436 (7)	88
B2	3576 (12)	−4408 (10)	2043 (9)	84
C51	3823 (9)	−5434 (10)	2290 (5)	90
C52	3370 (7)	−6030 (13)	2418 (7)	91
C53	3575 (9)	−6878 (13)	2652 (7)	103
C54	4220 (11)	−7172 (10)	2743 (7)	123
C55	4697 (8)	−6603 (13)	2642 (7)	103
C56	4508 (9)	−5752 (11)	2411 (6)	98
C61	3920 (6)	−4070 (10)	1520 (6)	81
C62	4075 (7)	−4697 (10)	1140 (8)	96
C63	4299 (10)	−4438 (15)	692 (11)	139
C64	4364 (10)	−3581 (20)	570 (9)	148
C65	4214 (8)	−2960 (12)	925 (9)	108
C66	3977 (7)	−3174 (11)	1388 (8)	93
C71	2745 (9)	−4338 (15)	1761 (7)	90
C72	2410 (11)	−3560 (13)	1823 (6)	87
C73	1712 (13)	−3457 (11)	1557 (8)	105
C74	1289 (8)	−4097 (17)	1188 (8)	104
C75	1607 (11)	−4836 (15)	1082 (8)	114
C76	2308 (13)	−4969 (9)	1363 (7)	93
C81	3911 (9)	−3844 (8)	2677 (6)	73
C82	3574 (7)	−3684 (9)	3121 (8)	85
C83	3848 (10)	−3168 (12)	3624 (7)	96
C84	4505 (12)	−2840 (12)	3756 (8)	117
C85	4854 (9)	−2965 (11)	3371 (10)	107
C86	4577 (10)	−3481 (10)	2848 (8)	85
N11	1916 (5)	231 (11)	−1620 (5)	85
N12	2357 (6)	406 (11)	−666 (5)	81
C17	2037 (8)	−158 (11)	−1056 (10)	103
C18	2478 (8)	1158 (13)	−950 (9)	117
C19	2183 (10)	1062 (11)	−1536 (10)	117
C10	1546 (6)	−212 (8)	−2182 (5)	96
N21	2212 (8)	−2571 (8)	157 (4)	83
N22	2279 (8)	−1106 (7)	217 (5)	86
C27	2600 (8)	−1842 (15)	166 (6)	84
C28	1651 (10)	−1421 (13)	280 (6)	97
C29	1596 (8)	−2283 (13)	244 (6)	100
C20	2400 (6)	−3500 (8)	98 (5)	108
N31	3377 (6)	−486 (10)	2187 (7)	88
N32	2979 (6)	114 (13)	1293 (5)	85
C37	3083 (8)	−641 (12)	1594 (11)	93
C38	3217 (8)	747 (10)	1696 (10)	95
C39	3465 (7)	391 (13)	2279 (8)	97
C30	3543 (6)	−1197 (8)	2655 (5)	113
N41	720 (9)	986 (7)	568 (8)	85
N42	1616 (6)	697 (7)	300 (8)	86
C47	1386 (11)	841 (9)	748 (6)	77
C48	1051 (14)	782 (10)	−201 (7)	92
C49	474 (8)	968 (10)	−36 (9)	94
C40	313 (5)	1167 (7)	978 (5)	93
N51	4771 (6)	−607 (8)	657 (7)	93
N52	3687 (7)	−215 (8)	361 (8)	93
C57	4272 (13)	−217 (10)	833 (7)	93
C58	3849 (9)	−621 (11)	−108 (7)	103
C59	4494 (10)	−844 (9)	66 (8)	82

Table 1 (cont.)

	x	y	z	U_{av}
C50	5481 (6)	−726 (8)	1030 (5)	119
N61	2936 (11)	3107 (8)	229 (5)	94
N62	2955 (10)	1680 (9)	410 (5)	86
C67	2584 (8)	2400 (20)	267 (6)	87
C68	3613 (11)	1945 (14)	416 (6)	101
C69	3594 (9)	2815 (15)	309 (7)	101
C60	2610 (5)	3973 (7)	62 (5)	97
C00	1269 (6)	−2750 (9)	−1948 (6)	134
Cl1	1087 (2)	−2418 (3)	−1292 (2)	180
Cl2	2150 (2)	−2530 (3)	−1782 (2)	181

Table 2. Selected bond lengths (Å) and angles (°)

Fe1–N12	2·228 (10)	N22–C27	1·320 (24)
Fe1–N22	2·203 (12)	N22–C28	1·426 (24)
Fe1–N32	2·174 (11)	N32–C37	1·325 (26)
Fe1–N42	2·225 (12)	N32–C38	1·325 (24)
Fe1–N52	2·204 (13)	N42–C47	1·309 (23)
Fe1–N62	2·210 (14)	N42–C48	1·367 (26)
N12–C17	1·270 (23)	N52–C57	1·347 (26)
N12–C18	1·382 (25)	N52–C58	1·397 (23)
		N62–C67	1·308 (30)
		N62–C68	1·407 (28)

N12–Fe1–N22	89·97 (50)	N52–Fe1–N62	94·98 (58)
N12–Fe1–N32	178·63 (51)	Fe1–N12–C17	127 (1·3)
N12–Fe1–N42	90·41 (57)	Fe1–N12–C18	124 (1·2)
N12–Fe1–N52	90·46 (57)	Fe1–N22–C27	129 (1·3)
N12–Fe1–N62	88·80 (51)	Fe1–N22–C28	127 (1·1)
N22–Fe1–N32	89·77 (55)	Fe1–N32–C37	127 (1·4)
N22–Fe1–N42	88·16 (50)	Fe1–N32–C38	126 (1·4)
N22–Fe1–N52	89·61 (52)	Fe1–N42–C47	129 (1·3)
N22–Fe1–N62	175·26 (64)	Fe1–N42–C48	126 (1·4)
N32–Fe1–N42	90·92 (57)	Fe1–N52–C57	128 (1·4)
N32–Fe1–N52	88·19 (58)	Fe1–N52–C58	126 (1·2)
N32–Fe1–N62	91·56 (57)	Fe1–N62–C67	132 (1·5)
N42–Fe1–N52	177·60 (45)	Fe1–N62–C68	121 (1·2)
N42–Fe1–N62	87·27 (56)		
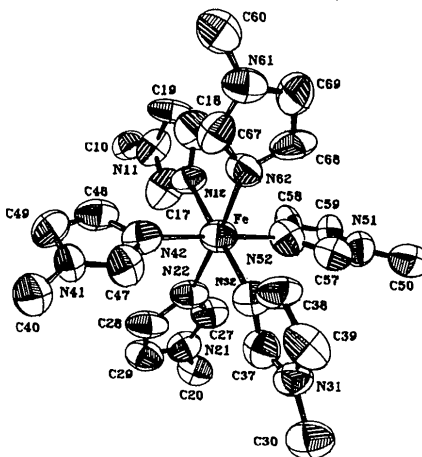
Fig. 1. ORTEP drawing of the cation in [Fe(C$_4$H$_6$N$_2$)$_6$](BPh$_4$)$_2$.·CH$_2$Cl$_2$ with 50% probability ellipsoids. H atoms are omitted.

minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma(F_o)^{-2}$. The final conventional residual index $R = 0·057$, and the associated weighted residual $wR = 0·063$, with a maximum shift/e.s.d. of 0·39. The minimum and maximum values in the final difference electron density map were $< 0·4$ e Å^{-3} in absolute value. The program ORTEP (Johnson, 1970) was used for molecular drawing.

Atomic parameters for the first and second co-ordination spheres of the cation are given in Table 1, selected bond distances and angles in Table 2.* A perspective view of the cation with atomic numbering is shown in Fig. 1.

Related literature. The hexakis(imidazole)Fe^{II} coordination sphere is also found in [Fe(C$_4$H$_6$N$_2$)$_6$][Fe$_2$(CO)$_8$] and [Fe(C$_5$H$_8$N$_2$)$_6$][Fe(CO)$_4$]$_2$ (Seel & Lehnert, 1980), and in 3Fe(C$_3$H$_3$N$_2$)$_2$.2C$_3$H$_4$N$_2$ (Lehnert & Seel, 1978). [Fe(C$_4$H$_6$N$_2$)$_6$](BPh$_4$)$_2$.CH$_2$Cl$_2$ is apparently unique in containing *only* this coordination sphere. 3Fe(C$_3$H$_3$N$_2$)$_2$.2C$_3$H$_4$N$_2$ contains both bridging imidazolato and terminal imidazole ligands.

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* A complete list of bond lengths and angles, anisotropic thermal parameters, H-atom parameters, selected least-squares planes and interplane angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51475 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Structure of [VCl₃(C₄H₈O)₂(OH)].C₄H₈O

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Abstract. Trichloro(hydroxo)bis(tetrahydrofuran)vanadium–tetrahydrofuran, C$_{12}$H$_{25}$Cl$_3$O$_4$V, M_r = 390·66, triclinic, $P\bar{1}$, a = 8·191 (15), b = 9·038 (5), c = 13·816 (12) Å, α = 91·35 (6), β = 106·39 (10), γ = 110·52 (1)°, V = 910 (3) Å^3, Z = 2, D_x = 1·42 Mg m^{-3}, Mo $K\alpha$ radiation, λ = 0·71073 Å, μ = 0·980 mm^{-1}, $F(000)$ = 406, T = 295 K, R = 0·088, wR = 0·093 for 2272 unique reflections [$I_o \geq 2\cdot5\sigma(I)$]. The V atom is octahedrally coordinated by the O atoms of two *trans* C$_4$H$_8$O (thf) ligands [V—O 2·018 (5), 2·043 (5) Å], three Cl atoms [V—Cl 2·322 (2), 2·347 (2) and 2·384 (2) Å] and one OH [V—O 2·046 (6) Å]. The OH ligand is hydrogen bonded to the O of a lattice thf. Both coordinated thf molecules are rotationally disordered about their V—O axes.

Experimental. [VCl₃(thf)₂(OH)].thf crystals were isolated as a byproduct of the preparation of (η-CH₃-C₅H₄)VCl₂(O) from VCl₂(thf)₂ (Sutin, 1988; Köhler & Prössdorf, 1977; Bottomley & Sutin, 1987). Light orange crystals were obtained. One of these, of dimensions 0·28 × 0·28 × 0·35 mm, was mounted on an Enraf–Nonius CAD-4 diffractometer. Lattice constants were obtained by accurate centering of 25 reflections in the range 15 < 2θ < 30°. Intensities were measured using the θ/2θ scan mode, to a 2θ$_{max}$ of 50° (h_{max} 9, k_{max} 10, l_{max} 15). Three standard reflections were monitored every hour. There was no significant change in their intensity. The intensities of 3193 unique reflections were measured, of which 2272 were judged as observed by the criteria that I > 2·5σ(I). An empirical absorption correction (*DIFABS*; Walker & Stuart, 1983) was made; relative transmission factors ranged from 0·63 to 1·44. The structure was solved using direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolson, 1980) and