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Bis(phenylmethanethiolato)(2,3,9,10-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetradecatetraene)iron(III) Hexafluorophosphate, $C_{28}H_{38}FeN_4S_2^+.PF_6^-$

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Abstract. $M_r = 695.58$, space group $P\bar{1}$, $a = 12.385$ (3), $b = 12.483$ (2), $c = 12.155$ (2) Å, $\alpha = 97.446$ (12), $\beta = 111.408$ (12), $\gamma = 63.960$ (13)°, $V = 1570.8$ (5) Å^3, $Z = 2$, $D_x = 1.471$ (5) Mg m^{-3}, Nb-filtered Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 0.738$ mm^{-1}, $F(000) = 722$, $T \sim 290$ K, $R = 0.082$, $R_w = 0.053$, $S = 1.38$ for 3622, 4040, 4040 reflections, 462 parameters. The average Fe–N(TIM) and Fe–S bond lengths are 1.928 (3) [6] (e.s.d. 0.003, scatter e.s.d. 0.006 of the average 1.928) and 2.288 (1) [2] Å. Comparison with other Fe(TIM) complexes seems to imply increased donation of electron density from the axial ligands (here sulfur) to Fe^{III}, and from Fe^{III} to the diimines of TIM. The two cations are both centrosymmetric, but have different axial ligand conformations, one fully extended, away from the TIM plane, and the other with the phenyls lying next to the TIM plane [Fe–S–C–C torsion angles 176.7 (3) and −80.2 (5)°; Fe–S–CH$_2$ 108.8 (2) and 114.4 (2)°].

Introduction. The crystal structures of two iron(II) complexes containing the macrocyclic ligand TIM (2,3,9,10-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetradecatetraene), [Fe(TIM)(NCCH$_3$)(CO)].(PF$_6$)$_2$ (McCandlish, Santarsiero, Rose & Lingafelter, 1979) and [Fe(TIM)(NCCH$_3$)$_2$].(PF$_6$)$_2$ (Smith, Santarsiero & Lingafelter, 1979), and one iron(III) complex, [Fe(TIM)(SCN)$_2$].PF$_6$ (Stenkamp & Jensen, 1980), have been determined. Here we describe a second Fe^{III}–TIM structure, [Fe(TIM)(SCH$_2$C$_6$H$_5$)$_2$].PF$_6$.

Experimental. Crystals dark-brown cubes, 0.10 mm on edge, prepared by Dr E. O. Fey; Picker FACS-I diffractometer. Lattice constants by least-squares refinement of the orientation matrix from two settings, '±2θ', 27 reflections, 2θ > 25°. Intensity measurements: 4081 reflections, ±h +k ±l, 2θ ≤ 45°, by 1.0° min^{-1} θ–2θ scans of 2θ width 1.6° plus α_1–α_2 angular dispersion, 20 s post-scan stationary-crystal-stationary-counter background counts fore and aft. 5 check reflections every 50 reflections, with no unusual variations, led to $q = 0.0057$ ('instability constant'), used in $1/w_{F^2} = (s + r^2b + q^2I^2)k^4/(Lp)^2$, $I = s − rb$, $F_o = k\sqrt{I/Lp}$, $k = 1.1781$ (12). Form factors from Stewart, Davidson & Simpson (1965) for H, and from *International Tables for X-ray Crystallography* (1962)

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Table 1. *Coordinates* $(\times 10^4)$ *and U_{eq} values* $(\text{Å}^2 \times 10^4)$

$U_{eq} = \frac{1}{3}$ trace **U**, where **U** is the diagonalized U_{ij} matrix.

	x	y	z	U_{eq}
Fe(1)	0	0	0	386
S(1)	702·8 (12)	268·0 (12)	1989·0 (10)	499
N(1A)	1300 (4)	−1603 (3)	363 (3)	410
N(2A)	1409 (4)	198 (4)	−155 (3)	432
C(1A)	2425 (5)	−1809 (4)	365 (4)	444
C(2A)	2464 (5)	−749 (5)	0 (4)	481
C(3A)	1241 (5)	1355 (5)	−521 (5)	688
C(4A)	268 (8)	2409 (5)	−137 (5)	714
C(5A)	−1110 (5)	2580 (4)	−716 (4)	565
C(6A)	3581 (5)	−2979 (5)	682 (5)	762
C(7A)	3601 (5)	−807 (5)	−222 (5)	803
C(8A)	−581 (5)	1514 (5)	2360 (4)	687
C(91A)	−188 (5)	1683 (4)	3686 (4)	501
C(92A)	−764 (5)	1449 (5)	4341 (5)	637
C(93A)	−438 (7)	1635 (6)	5548 (6)	810
C(94A)	456 (8)	2047 (6)	6073 (5)	914
C(95A)	1076 (7)	2255 (6)	5441 (6)	966
C(96A)	740 (6)	2091 (5)	4249 (5)	791
Fe(2)	5000	5000	5000	425
S(2)	3704·1 (13)	6785·3 (12)	3962·7 (11)	546
N(1B)	4046 (4)	4386 (3)	3664 (3)	474
N(2B)	3638 (4)	5170 (3)	5522 (4)	463
C(1B)	2955 (5)	4481 (4)	3661 (5)	564
C(2B)	2746 (5)	4887 (5)	4784 (5)	557
C(3B)	3633 (5)	5569 (5)	6721 (5)	634
C(4B)	4190 (6)	6469 (5)	7150 (5)	684
C(5B)	5597 (6)	6015 (5)	7415 (4)	671
C(6B)	1952 (6)	4261 (5)	2621 (5)	829
C(7B)	1636 (5)	4897 (5)	5034 (5)	830
C(8B)	4510 (5)	7724 (5)	4042 (5)	634
C(91B)	4708 (6)	8419 (5)	5141 (5)	577
C(92B)	3740 (7)	9061 (6)	5602 (6)	819
C(93B)	3950 (11)	9704 (7)	6588 (9)	1290
C(94B)	5125 (19)	9737 (12)	7119 (10)	1742
C(95B)	6063 (12)	9101 (11)	6697 (13)	1629
C(96B)	5872 (7)	8466 (6)	5697 (8)	1036
P	2443·1 (16)	3996·1 (16)	8821·6 (14)	621
F(1)	3191 (3)	3420 (3)	7937 (3)	1126
F(6)	1724 (4)	4590 (4)	9719 (3)	1296
F(2)	1601 (16)	5148 (13)	8077 (18)	1550*
F(23)	1248 (13)	4223 (25)	7662 (16)	1039†
F(3)	1380 (12)	3543 (15)	8242 (12)	1102*
F(34)	2574 (36)	2731 (18)	8847 (23)	1381†
F(4)	3232 (14)	2816 (11)	9653 (12)	1322*
F(45)	3764 (17)	3696 (30)	9861 (13)	1100†
F(5)	3467 (13)	4433 (17)	9503 (16)	1489*
F(25)	2326 (34)	5277 (21)	8534 (26)	1207†

* Partial population = 0·65.
† Partial population = 0·35.

for the other atoms, including f' and f'' for all but H atoms. Structure determination: Patterson map and Fourier difference maps (*XRAY*76; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), $P\bar{1}$. Final refinement (*CRYRM*; Duchamp, Trus & Westphal, 1964): full-matrix least squares, on $|F|^2$, 4040 reflections (the 41 of least 2θ omitted because the scans overlapped the Nb K edge); anisotropic Gaussian amplitudes for non-H atoms, PF_6^- rotational disorder (set at 65:35) about the F(1)—P—F(6) axis and disordered CH_3's except at C(6A) from ΔF maps, the other H's at calculated positions, all H's isotropic with $U = 0·10$ Å^2. Final cycle: $S = 1·38$, $R_F = 0·082$ (3622 reflections of positive net count), $R_w = [\sum w_{F^2}(F_o^2 - F_c^2)^2/(2\sum w_F F_o^2)]^{1/2} = 0·053$ (4040 reflections), final $|\Delta\rho|_{max}$ 0·47 e Å^{-3}, except for 0·64 e Å^{-3} at Fe(2), Δ/σ in final cycle: 0·05 except for the disordered F's [max. for them 0·4 for $x_{F(4)}$]; $R_F = 0·045$, $R_w = 0·046$ for the 2350 reflections of $F^2 > 2\sigma_{F^2}$ (final coordinates,

Table 1).* No corrections for absorption $(\mu d \simeq 0·074)$ or extinction.

Discussion. The benzyl groups are deployed quite differently in the two centrosymmetric cations (Fig. 1), fully extended with rings almost perpendicular to the TIM plane in A, but flat-on, almost parallel to TIM, in B [Fe—S—C(8)—C(91) 176·7 (3) vs 80·2 (5)°]. The cations are closely similar in most other respects, including the azimuth of C(8) [torsion angles in A C(8)—S—Fe—N(1') 22·8 (2), C(8)—S—Fe—N(2') −57·2 (2)°; in B 39·5 (2), −40·6 (2)°]. However, several minor differences indicate strain in B: Fe—S—C(8) 5·6° greater in B than A, where it is perhaps already unusually large [114·4 (2), 108·8 (2)°], and S—C(8)—C(91) 5·1° greater in B—and clearly abnormal [115·9 (4), 110·8 (4)°]; in addition, S leans away from N(1'), a little more in B than A {[N(1), N(2), N(1'), N(2')]—Fe—S = 83·9, 89·7, 96·1, 90·4° in B vs 85·8, 90·7, 94·2, 89·3° in A, e.s.d.'s ~0·15°}. If all these angles [at C(8), S, and Fe] were normal the close intramolecular contacts between benzyl and TIM in B [notably C(8)···N(2'), N(1'), C(2') 3·305 (7), 3·469 (7), 3·485 (8); C(91)···N(1'), C(1') 3·419 (8), 3·563 (9); C(92)···C(4) 3·681 (10); C(95)···C(6') 3·833 (16); C(96)···C(1'), C(6') 3·388 (10), 3·572 (11) Å] would be shortened intolerably—by more than 0·5 Å. In B the torsions around C(8)—C(91) sum to 182·5 (14)° [in A the sum is 180·9 (11)°] in the sense to suggest that C(92) and C(96) are indeed forced against their TIM contacts by C(91) in consequence of the angle strains at C(8) and S. By and large, this interpretation is confirmed by the deviations from the phenyl least-squares plane and from the FeN$_4$ plane. Phenyl: C(8) 0·036, C(91)—C(96) −0·002, −0·001, −0·006, 0·015, −0·018, 0·011, Fe(2) 3·266 Å. TIM: C(3) −0·12, C(4) 0·57, C(5) −0·05, C(1') −0·14, C(2') −0·07, C(6') −0·41, C(7') −0·02, S(2) 2·3 Å.

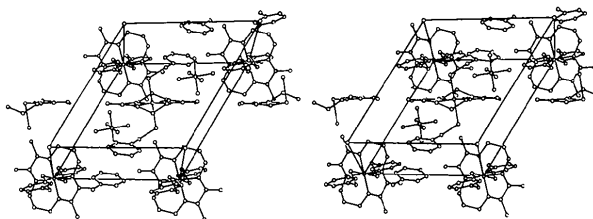Fig. 1. Stereo partial view of the structure. Molecule B is at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

Table 2. *Comparison of important structural features* (Å,°) *in* Fe(TIM) *compounds*

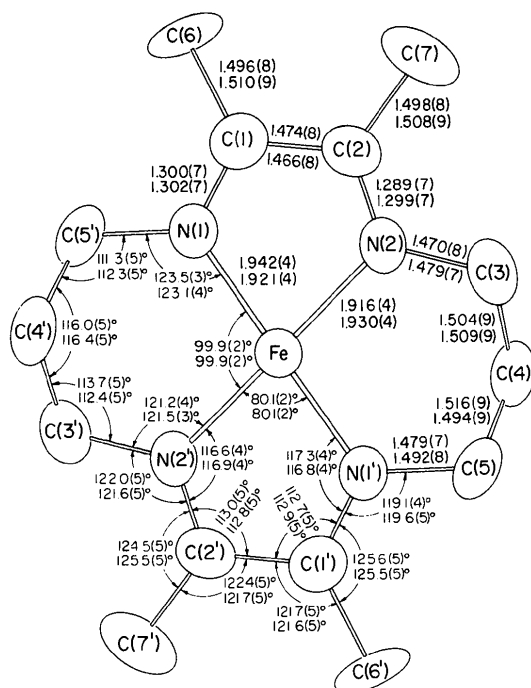|	Fe(TIM)(SCH$_2$Ph)$_2^+$	Fe(TIM)(SCN)$_2^+$	Fe(TIM)(NCCH$_3$)$_2^{2+}$	Fe(TIM)(NCCH$_3$)(CO)$^{2+}$
Fe—N(TIM)	1·928 (2)|6|	1·950 (3)	1·948 (1)	1·954 (1)
Fe—X_{axial}	S 2·288 (1)|2|	S 2·328 (2)	N 1·929 (1)	N 1·976 (3)
N=C	1·298 (4)|3|	1·280 (4)	1·291 (2)	1·289 (2)
C—C(imine)	1·470 (8)|4|	1·491 (6)	1·477 (4)	1·480 (4)
N—CH$_2$	1·480 (5)|5|	1·493 (5)	1·475 (3)	1·467 (3)
CH$_2$—CH$_2$	1·506 (6)|5|	1·509 (5)	1·505 (3)	1·512 (4)
C—CH$_3$	1·503 (4)|4|	1·500 (5)	1·516 (4)	1·519 (3)
N···N(TIM)	2·481 (4)|3|	2·504 (5)	2·524 (3)	2·534 (3)
	2·952 (4)|3|	2·990 (5)	2·968 (3)	2·973 (3)
N$_{TIM}$···X_{axial}	2·828 (5)	2·956 (4)	2·712 (3)	2·722 (4)
range	3·142 (5)	3·115 (4)	2·774 (2)	2·755 (4)
C(3)—C(4)—C(5)	116·2 (4)|2|	115·8 (4)	115·5 (2)	116·4 (4)
Fe N CH$_2$ CH$_2$	31·6|12|	30	40	40
Fe—X_{axial}—C	111·6 (1)|28|	104	178	176

Fig. 2. Bond lengths (Å) and angles; upper entries for *A*, lower entries for *B*. Not included: Fe—S 2·2856 (10), 2·2898 (10) Å; S—C(8) 1·822 (6), 1·818 (6) Å; C(8)—C(91) 1·520 (8), 1·499 (9) Å; Fe—S—C(8) 108·8 (2), 114·4 (2)°; S—C(8)—C(91) 110·8 (4), 115·9 (4)°.

The phenyl deviations C(91)–C(96) are very small (scatter e.s.d. 0·012 Å), and only a trifle greater than for *A* (0·010 Å), while the C(8) is a bit greater for *A* than for *B*. The TIM deviations are more impressive, however: r.m.s. 0·186 Å for *B* [excepting C(4)] *vs* 0·104 Å for *A*. Finally, the pattern of TIM torsions has nearly C_{2v} symmetry in *A*, but is twisted a few degrees in *B* as if to rotate the up-turned C(4) away from the phenyl group. The *B* phenyl appears to be snapped into its niche (Fig. 1), where its intermolecular contacts all seem reasonable in relation to the usual van der Waals radii and to the other intermolecular contacts in the structure, none of which seem abnormal. (The H

contacts were not examined.) The S—C(8) torsion angle could be changed to relieve the intramolecular strain, but only at the expense of shortening several intermolecular contacts, and we have no explanation for the large mainly in-plane *U*'s of the distal phenyl carbons in *B*.

The corresponding bond lengths and angles in the TIM's of *A* and *B* are nearly equal (Fig. 2, Table 2), with r.m.s. deviations (0·010 Å, 0·6°), and both have similarly good 2/*m* symmetry (not just $\bar{1}$) in bond lengths and, with a few exceptions, *e.g.* Fe—N(1)—C(5'), in bond angles also. Several structural features are summarized in Table 2 for each of the four Fe(TIM) compounds. Three of the important average lengths of potentially conjugated bonds are *shorter* in the thiolate complex than in the thiocyanate, (1) Fe—N(TIM) by 0·022 (4) Å, (2) Fe—S by 0·040 (3) Å, and (3) C—C in the TIM diimine unit by 0·021 (14) Å, and one is longer, N=C, by 0·018 (8) Å, perhaps implying increased donation of electron density from the axial ligands to the iron atom, and from the iron atom into the diimine unit. Note that our Fe—S average is in the range observed for tetrahedral Fe^{III}—S$_4$ complexes, *e.g.* [Fe(S$_2$–*o*-xylyl)$_2$]$^-$ 2·25–2·28 Å (Lane, Ibers, Frankel, Papaefthymiou & Holm, 1977).

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