

- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.  
 Stoe & Cie (1988a). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.  
 Stoe & Cie (1988b). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

*Acta Cryst.* (1995). **C51**, 2244–2246

**{Tris[4-(2-pyridyl)-3-aza-3-butenyl]-amine}iron(II) Bis(hexafluorophosphate), [Fe(py<sub>3</sub>tren)](PF<sub>6</sub>)<sub>2</sub>**

KAMAL BOUBEKEUR

*Laboratoire de Physique des Solides, CNRS-URA 02, Université Paris-Sud, 91405 Orsay, France*

ALAIN DEROCHE, FRANCOIS LAMBERT AND  
 IRENE MORGENSTERN-BADARAU\*

*Laboratoire de Chimie Bioorganique et Bioinorganique, Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud, 91405 Orsay, France*

(Received 6 March 1995; accepted 9 May 1995)

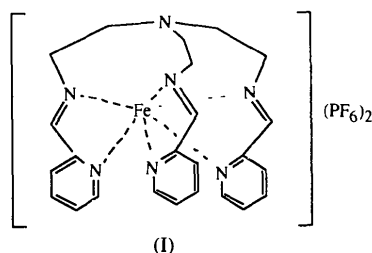
**Abstract**

The coordination polyhedron of the Fe<sup>II</sup> ion in the title compound, [Fe(C<sub>24</sub>H<sub>27</sub>N<sub>7</sub>)](PF<sub>6</sub>)<sub>2</sub>, is best described as a trigonal antiprism twisted 6° towards a trigonal prism. The tris[4-(2-pyridyl)-3-aza-3-butenyl]amine ligand coordinates to the metal centre through the three pyridine and three imino N atoms, each set of atoms forming two parallel ideal equilateral triangles; the metal ion is located between these two planes. The average values for the Fe—N<sub>pyridine</sub> and the Fe—N<sub>imino</sub> bond lengths are 1.981 and 1.950 Å, respectively. The tripodal bridging amine N atom lies on the pseudo ternary axis of the molecule and is situated 3.427 (7) Å from the Fe centre.

**Comment**

The potentially heptadentate tripodal ligand tris[4-(2-pyridyl)-3-aza-3-butenyl]amine (py<sub>3</sub>tren) has been found to form iron(II) and manganese(II) complexes characterized by sixfold coordination of the metal ion (Kichner *et al.*, 1987). As part of our continuing studies involving such hindered polydentate ligands and our general interest in their complexes, which may be proposed as iron or manganese superoxide mimics, we have found that the complex [Fe(py<sub>3</sub>tren)](PF<sub>6</sub>)<sub>2</sub> can be formed in two different ways: (a) by the direct mixing of py<sub>3</sub>tren with FeCl<sub>2</sub> and NH<sub>4</sub>PF<sub>6</sub> in methanol to give

compound (I), and (b) by the reaction of a methanolic solution of FeCl<sub>3</sub> with the polyamine ligand tris[4-(2-pyridylmethyl)-2-aminoethyl]amine (TPAA), in the presence of NH<sub>4</sub>PF<sub>6</sub>, under an air atmosphere to give compound (II). This reaction involves the oxidation of the TPAA ligand through a metal-assisted oxidative dehydrogenation.



We have shown recently that TPAA can form a heptadentate manganese(II) complex (MnTPAA) and have performed the first crystallographic characterization of the structure of this ligand (Deroche *et al.*, 1995). In the present paper, we report the crystal structure of (I). An ORTEPII (Johnson, 1976) plot of the [Fe(py<sub>3</sub>tren)]<sup>2+</sup> ion is shown in Fig. 1. The coordination polyhedron of the iron(II) ion is best described as a trigonal antiprism twisted 6° towards a trigonal prism. The Fe atom is bonded to three pyridine N atoms [Fe—N<sub>2</sub>, Fe—N<sub>4</sub> and Fe—N<sub>6</sub> are 1.983 (3), 1.980 (4) and 1.979 (3) Å, respec-

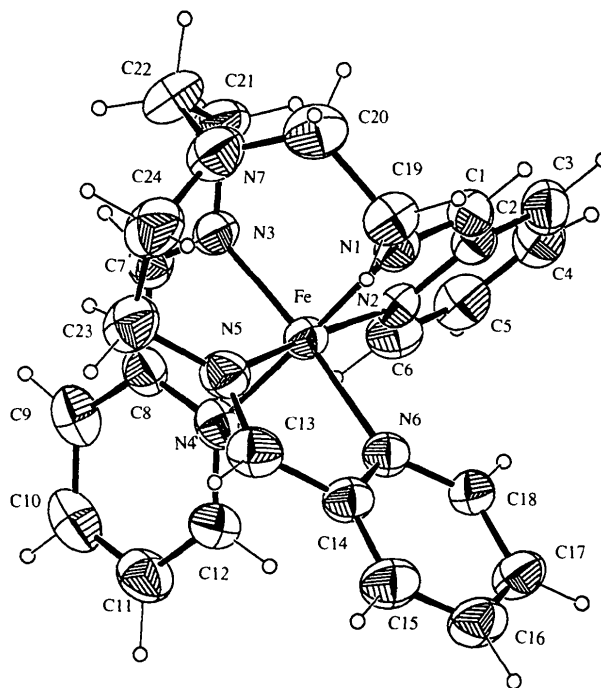


Fig. 1. An ORTEPII (Johnson, 1976) drawing of the [Fe(C<sub>24</sub>H<sub>27</sub>N<sub>7</sub>)]<sup>2+</sup> cation with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

tively] and three imino N atoms [Fe—N1, Fe—N3 and Fe—N5 are 1.952 (4), 1.953 (3) and 1.946 (4) Å, respectively]. The tripodal bridging amine N atom, N7, lies on the pseudo ternary axis of the molecule and is situated 3.427 (7) Å from the Fe centre. The Fe...N7 distance is too long for any interactions between the atoms to be considered. This crystal structure is very similar to the structure of [Fe(py<sub>3</sub>tren)](BF<sub>4</sub>)<sub>2</sub> reported previously (Kichner *et al.*, 1987); this complex was obtained by mixing py<sub>3</sub>tren with FeCl<sub>2</sub> and NaBF<sub>4</sub> in methanol. The presence of the counter anion BF<sub>4</sub><sup>-</sup> instead of PF<sub>6</sub><sup>-</sup> does not induce significant changes in the structure. Nevertheless, in order to perform a reliable comparison of (I) and (II), which are surprisingly different, it was necessary to obtain the molecular cationic complex [Fe(py<sub>3</sub>tren)]<sup>2+</sup> crystallized with the same counter anion, PF<sub>6</sub><sup>-</sup>. The structure of (II) and its comparison with (I) are undergoing further study.

### Experimental

To a stirred solution containing 0.294 g (0.71 mmol) of py<sub>3</sub>tren in methanol (15 ml) was added a solution of 0.140 g (0.71 mmol) of FeCl<sub>2</sub>·4H<sub>2</sub>O dissolved in methanol (5 ml). The red solution that formed was stirred for 1 h at room temperature under air atmosphere, after which 0.347 g (2.13 mmol) of NH<sub>4</sub>PF<sub>6</sub> in methanol (5 ml) was added to induce precipitation of the complex. The solution was filtered and the complex recrystallized from a 1:1 CH<sub>3</sub>OH/acetone solution, yielding 0.42 g (78%) of (I), crystals of which were suitable for X-ray crystallographic analysis.

#### Crystal data

[Fe(C<sub>24</sub>H<sub>27</sub>N<sub>7</sub>)](PF<sub>6</sub>)<sub>2</sub>

*M<sub>r</sub>* = 759.29

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 14.806 (2) Å

*b* = 10.677 (2) Å

*c* = 19.669 (5) Å

*β* = 108.55 (2)°

*V* = 2947.8 (10) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.71 Mg m<sup>-3</sup>

Mo *Kα* radiation

*λ* = 0.71073 Å

Cell parameters from 25 reflections

*θ* = 8.3–17.5°

*μ* = 0.720 mm<sup>-1</sup>

*T* = 293 K

Parallelepiped

0.33 × 0.21 × 0.09 mm

Black-red

*R*<sub>int</sub> = 0.009

*θ*<sub>max</sub> = 27°

*h* = 0 → 18

*k* = 0 → 13

*l* = -24 → 22

3 standard reflections

frequency: 60 min

intensity decay: 1.2%

#### Data collection

Enraf-Nonius CAD-4F

diffractometer

*ω*/*2θ* scans

Absorption correction:

*ψ* scans

*T*<sub>min</sub> = 0.92, *T*<sub>max</sub> = 1.00

6292 measured reflections

5963 independent reflections

2802 observed reflections

[*I* > 3σ(*I*)]

#### Refinement

Refinement on *F*

*R* = 0.051

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*) + 0.0016*F<sub>o</sub>*<sup>2</sup>]

(Δ/*σ*)<sub>max</sub> < 0.001

*wR* = 0.061

*S* = 1.854

2802 reflections

416 parameters

H-atom parameters not

refined

Δ*ρ*<sub>max</sub> = 0.63 e Å<sup>-3</sup>

Δ*ρ*<sub>min</sub> = -0.38 e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$B_{eq} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
Fe	-0.27522 (5)	0.24738 (8)	0.19130 (4)	2.84 (1)
P1	0.0784 (1)	0.2261 (2)	0.5988 (1)	4.87 (4)
P2	-0.5484 (1)	0.2315 (2)	0.3685 (1)	4.95 (4)
F1	-0.0323 (3)	0.2281 (5)	0.5703 (3)	8.9 (1)
F2	0.1896 (3)	0.2185 (6)	0.6259 (3)	12.7 (12)
F3	0.0755 (4)	0.1572 (7)	0.5291 (3)	13.7 (2)
F4	0.0741 (4)	0.1015 (5)	0.6385 (3)	11.9 (2)
F5	0.0822 (4)	0.3482 (5)	0.5588 (3)	13.8 (2)
F6	0.0798 (5)	0.2975 (7)	0.6648 (3)	17.1 (3)
F7	-0.4434 (3)	0.2807 (4)	0.4045 (3)	8.2 (1)
F8	-0.6522 (3)	0.1801 (5)	0.3333 (3)	8.9 (1)
F9	-0.5266 (4)	0.1169 (5)	0.4164 (3)	14.9 (2)
F10	-0.5696 (4)	0.3486 (5)	0.3166 (3)	11.4 (2)
F11	-0.5169 (3)	0.1631 (5)	0.3084 (3)	10.0 (1)
F12	-0.5828 (3)	0.3145 (5)	0.4197 (2)	10.5 (1)
N1	-0.3295 (3)	0.3756 (4)	0.2375 (2)	3.1 (1)
N2	-0.4122 (3)	0.2084 (4)	0.1458 (2)	2.7 (1)
N3	-0.2698 (3)	0.1144 (4)	0.2607 (2)	3.1 (1)
N4	-0.2296 (3)	0.1092 (4)	0.1436 (2)	3.3 (1)
N5	-0.1433 (3)	0.3006 (5)	0.2325 (2)	3.6 (1)
N6	-0.2707 (3)	0.3728 (4)	0.1184 (2)	3.0 (1)
N7	-0.1807 (4)	0.3049 (5)	0.3716 (3)	4.7 (1)
C1	-0.4211 (4)	0.3788 (5)	0.2183 (3)	3.6 (1)
C2	-0.4715 (4)	0.2845 (5)	0.1677 (3)	3.2 (1)
C3	-0.5699 (4)	0.2708 (6)	0.1438 (3)	4.2 (1)
C4	-0.6087 (4)	0.1747 (6)	0.0963 (3)	4.3 (2)
C5	-0.5492 (4)	0.0967 (6)	0.0754 (3)	4.2 (2)
C6	-0.4524 (4)	0.1160 (5)	0.1004 (3)	3.8 (1)
C7	-0.2491 (4)	0.0054 (5)	0.2428 (3)	3.7 (1)
C8	-0.2221 (4)	-0.0030 (5)	0.1782 (3)	3.3 (1)
C9	-0.1926 (4)	-0.1106 (6)	0.1535 (3)	4.4 (2)
C10	-0.1643 (4)	-0.1052 (6)	0.0929 (3)	4.9 (2)
C11	-0.1680 (4)	0.0093 (6)	0.0589 (3)	4.4 (2)
C12	-0.2019 (4)	0.1131 (6)	0.0846 (3)	4.0 (1)
C13	-0.1138 (4)	0.3822 (6)	0.1964 (3)	3.9 (1)
C14	-0.1850 (4)	0.4284 (5)	0.1308 (3)	3.4 (1)
C15	-0.1659 (4)	0.5152 (6)	0.0856 (3)	4.4 (2)
C16	-0.2394 (4)	0.5496 (6)	0.0254 (3)	4.5 (2)
C17	-0.3274 (4)	0.4968 (6)	0.0127 (3)	4.2 (2)
C18	-0.3416 (4)	0.4080 (5)	0.0593 (3)	3.4 (1)
C19	-0.2767 (4)	0.4695 (5)	0.2895 (3)	3.9 (1)
C20	-0.2405 (5)	0.4128 (6)	0.3649 (3)	4.6 (2)
C21	-0.2942 (4)	0.1260 (6)	0.3273 (3)	4.2 (1)
C22	-0.2124 (5)	0.1829 (6)	0.3882 (3)	4.6 (2)
C23	-0.0738 (4)	0.2523 (7)	0.2991 (3)	4.6 (1)
C24	-0.0863 (5)	0.3160 (7)	0.3654 (3)	5.3 (2)

Table 2. Selected geometric parameters (Å, °)

Fe—N1	1.952 (4)	Fe—N4	1.980 (4)
Fe—N3	1.953 (3)	Fe—N6	1.979 (3)
Fe—N5	1.946 (4)	Fe—N7	3.427 (7)
Fe—N2	1.983 (3)		
N1—Fe—N2	81.0 (1)	N2—Fe—N6	94.6 (1)
N1—Fe—N6	88.7 (1)	N2—Fe—N3	88.4 (1)
N1—Fe—N5	96.2 (2)	C20—N7—C24	120.8 (4)
N1—Fe—N4	175.3 (2)	C20—N7—C22	120.3 (4)
N1—Fe—N3	96.6 (1)	C22—N7—C24	118.8 (4)

The empirical absorption correction was based on azimuthal *ψ* scans of three reflections having a Eulerian *χ* near 90° (*k* > 100°) around the diffraction vector. The structure was

solved by direct methods using *MULTAN11/82* (Main *et al.*, 1982) and refined by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic displacement parameters for non H-atoms. All H atoms were found from a difference Fourier map and included in the structure-factor calculations. All calculations were performed on DEC MicroVAX II and IBM RS/6000 computers using the *Enraf-Nonius SDP-Plus* (Frenz, 1985) and *Xtal3.2* (Hall, Flack & Stewart, 1992) systems. Molecular graphics were prepared using *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and root-mean-square amplitudes have been deposited with the IUCr (Reference: NA1171). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Deroche, A., Morgenstern-Badarau, I., Cesario, M., Guilhem, J., Keita, B. & Nadjo, L. (1995). In preparation.
- Frenz, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.
- Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal3.2 Reference Manual*. Univs. of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kichner, R. M., Mealli, C., Bailey, M., Howe, N., Torre, L. P., Wilson, L. J., Andrews, L. C., Rose, N. J. & Lingafelter, E. C. (1987). *Coord. Chem. Rev.* **77**, 89–163.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

*Acta Cryst.* (1995). **C51**, 2246–2249

## *fac*-Tris(isothiocyanato)tris(triphenylphosphine oxide)iron(III) at 80 K

ZOFIA OLEJNIK AND TADEUSZ LIS

*Institute of Chemistry, University of Wrocław,  
ul. Joliot-Curie 14, 50-383 Wrocław, Poland*

IVETA ONDREJKOVIČOVÁ

*Department of Inorganic Chemistry, Slovak Technical  
University, 9 Radlinského St., 812 37 Bratislava,  
Slovakia*

(Received 21 February 1995; accepted 15 May 1995)

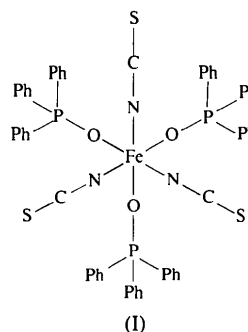
## Abstract

The iron(III) complex [Fe(NCS)<sub>3</sub>(C<sub>18</sub>H<sub>15</sub>PO)<sub>3</sub>] crystallizes in space group *R*3. One complex molecule with no crystallographically imposed symmetry and one-third of

another molecule arranged about a threefold axis are contained in the asymmetric unit. Both molecules have almost the same geometry for the octahedral FeO<sub>3</sub>N<sub>3</sub> chromophores, but opposite chirality of the arrangement of the ligands around the Fe atoms.

## Comment

Iron(III) triphenylphosphine oxide complexes of composition FeX<sub>3</sub>(OPPh<sub>3</sub>)<sub>2</sub> (X = Cl<sup>-</sup>, Br<sup>-</sup> or SCN<sup>-</sup>) act as oxidation catalysts of PPh<sub>3</sub> with O<sub>2</sub> in acetonitrile solutions (Ondrejkočová, Vančová & Ondrejovič, 1983, 1991). These complexes show different catalytic activity, which depends not only on the redox potentials X<sub>2</sub>/X<sup>-</sup> but also on their crystal structures. Chloro and bromo complexes have the ionic structure [FeX<sub>2</sub>(OPPh<sub>3</sub>)<sub>4</sub>][FeX<sub>4</sub>] (Durčanská, Głowiak, Kožišek, Ondrejkočová & Ondrejovič, 1989; Durčanská, Głowiak, Gyepes, Ondrejkočová & Ondrejovič, 1991) and [Fe(NCS)<sub>3</sub>(OPPh<sub>3</sub>)<sub>2</sub>] has a non-ionic structure (Cotton & Gibson, 1971).



The title compound, (I), the crystal structure of which we present here, exhibits catalytic properties similar to those of [Fe(NCS)<sub>3</sub>(OPPh<sub>3</sub>)<sub>2</sub>] (Vančová, Ondrejkočová & Ondrejovič, 1984). The unit cell contains twelve molecules of [Fe(NCS)<sub>3</sub>(OPPh<sub>3</sub>)<sub>3</sub>], in each of which three NCS<sup>-</sup> and three OPPh<sub>3</sub> ligands are coordinated at facial sites octahedrally around the Fe atom. Three of the complex molecules (type *A*) have crystallographic threefold symmetry and the remaining nine (type *B*), situated at general positions, have approximate threefold symmetry. In Fig. 1 an *ORTEPII* (Johnson, 1976) view of both molecules projected along the *c* axis is presented. As can be seen, molecules *A* and *B* have opposite chirality, probably imposed by the crystal packing and/or the arrangement of triphenylphosphine oxide ligands. More pronounced differences between the independent molecules *A* and *B* are observed in the Fe—N—C and Fe—O—P angles (see Table 2), which are more acute in *A*. Both molecules have very similar coordination octahedra, the weighted r.m.s. deviation for the FeO<sub>3</sub>N<sub>3</sub> cores being 0.0129 Å. All Fe—N and Fe—O bond distances are almost equal and the N—Fe—N and O—Fe—O bond angles do not exhibit deviations from