

Zofia Olejnik,<sup>a\*</sup> Tadeusz Lis,<sup>a</sup>  
Iveta Ondrejková,<sup>b</sup> Jozef  
Malo<sup>b</sup> and Sylvia Galková<sup>b</sup><sup>a</sup>Faculty of Chemistry, University of Wrocław,  
14 Joliot-Curie St, 50-383 Wrocław, Poland,  
and <sup>b</sup>Department of Inorganic Chemistry, Slovak  
Technical University, Radlinského 9, 812 37  
Bratislava, SlovakiaCorrespondence e-mail:  
olej@wchuwr.chem.uni.wroc.pl

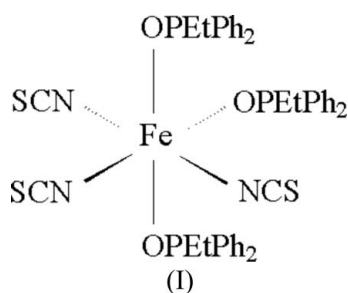
## Key indicators

Single-crystal X-ray study  
 $T = 100$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
Disorder in main residue  
 $R$  factor = 0.047  
 $wR$  factor = 0.114  
Data-to-parameter ratio = 24.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**mer-Tris(ethyldiphenylphosphine oxide)tris(iso-  
thiocyanato)iron(III)**

The title compound,  $[\text{Fe}(\text{NCS})_3(\text{C}_{14}\text{H}_{15}\text{OP})_3]$ , adopts a meridional coordination of the three  $\text{NCS}^-$  ligands and three  $\text{OPEtPh}_2$  ligands. The  $\text{Fe}-\text{N}$  and  $\text{Fe}-\text{O}$  bond lengths fall in the range 1.982 (2)–2.045 (2) Å, and the bond angles around the  $\text{Fe}^{3+}$  centre deviate only slightly from an ideal octahedral geometry. The three  $\text{OPEtPh}_2$  ligands have similar geometries to each other and adopt the same general conformation with differences in the relative orientations of the phenyl groups. The  $\text{NCS}^-$  ligands are almost linear and the  $\text{Fe}-\text{N}-\text{C}$  angles range from 170.78 (17) to 177.56 (17)°. In contrast, the  $\text{Fe}-\text{O}-\text{P}$  angles show a great variation with two angles close to 180° [166.29 (10) and 171.21 (10)°] and the angles corresponding to a disordered  $\text{OPEtPh}_2$  ligand far from 180° [137.0 (10) and 137.9 (5)°]. Both the disorder and the variations in the angles around the N and O atoms seem to result from weak intermolecular  $\text{C}-\text{H}\cdots\text{S}$  interactions.

## Comment

The structure of the title compound, (I), is shown below. Dimensions are listed in Table 1.



Unlike *fac*-tris(isothiocyanato)tris(triphenylphosphine oxide)iron(III) (Olejnik *et al.*, 1995), the title compound,  $[\text{Fe}(\text{NCS})_3(\text{C}_{14}\text{H}_{15}\text{OP})_3]$ , adopts a meridional coordination of the three  $\text{NCS}^-$  ligands and three  $\text{OPEtPh}_2$  ligands. The  $\text{Fe}-\text{N}$  and  $\text{Fe}-\text{O}$  bond lengths fall in the range 1.982 (2)–2.045 (2) Å, and the bond angles around the  $\text{Fe}^{3+}$  centre deviate only slightly from an ideal octahedral geometry. The three  $\text{OPEtPh}_2$  ligands have similar geometries to each other and adopt the same general conformation with differences in the relative orientations of the phenyl groups. The  $\text{NCS}^-$  ligands are almost linear and the  $\text{Fe}-\text{N}-\text{C}$  angles range from 170.78 (17) to 177.56 (17)°. In contrast, the  $\text{Fe}-\text{O}-\text{P}$  angles show a great variation with two angles close to 180° [166.29 (10) and 171.21 (10)°] and the angles corresponding to a disordered  $\text{OPEtPh}_2$  ligand far from 180° [137.0 (10) and 137.9 (5)°]. Both the disorder and the variations in the angles around the N and O atoms seem to result from weak intermolecular  $\text{C}-\text{H}\cdots\text{S}$  interactions (Table 2).

Received 5 September 2005

Accepted 10 October 2005

Online 19 October 2005

## Experimental

The title compound was obtained in two steps. First, an acetonitrile solution of  $\text{Fe}(\text{SCN})_3$  was prepared by mixing acetonitrile solutions of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{KSCN}$  in stoichiometric amounts; the insoluble  $\text{KCl}$  formed during the reaction was filtered off. An acetonitrile solution (10 ml) of ethyldiphenylphosphine oxide (0.690 g, 3.00 mmol) was then added to the acetonitrile solution (30 ml) of  $\text{Fe}(\text{SCN})_3$  (1.00 mmol) and the mixture was refluxed. After cooling, dark-red crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation.

### Crystal data

$[\text{Fe}(\text{NCS})_3(\text{C}_{14}\text{H}_{15}\text{OP})_3]$   
 $M_r = 920.78$   
 Monoclinic,  $P2_1/c$   
 $a = 14.565$  (3) Å  
 $b = 16.839$  (3) Å  
 $c = 20.092$  (4) Å  
 $\beta = 110.47$  (3)°  
 $V = 4616.6$  (18) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.325$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 27191 reflections  
 $\theta = 4.5$ – $30.0$ °  
 $\mu = 0.61$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 Plate, dark red  
 $0.25 \times 0.25 \times 0.10$  mm

### Data collection

Kuma KM-4 CCD  $\kappa$ -geometry diffractometer  
 $\omega$  scans

Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2003)], analytical numeric absorption using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]

$T_{\min} = 0.852$ ,  $T_{\max} = 0.946$   
 57584 measured reflections  
 13417 independent reflections  
 8964 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.042$   
 $\theta_{\text{max}} = 30.0$ °  
 $h = -20 \rightarrow 20$   
 $k = -23 \rightarrow 23$   
 $l = -25 \rightarrow 28$

### Refinement

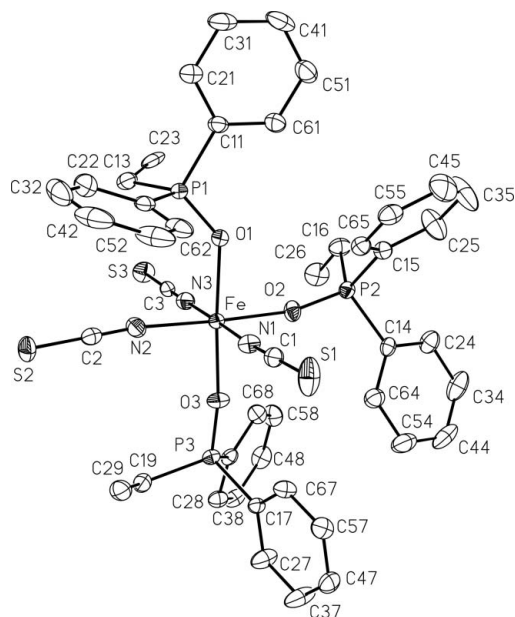
Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.114$   
 $S = 1.01$   
 13417 reflections  
 555 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0552P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.90$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.35$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

|                  |            |               |             |
|------------------|------------|---------------|-------------|
| Fe—O2            | 1.982 (2)  | O2—P2         | 1.503 (2)   |
| Fe—O3            | 1.990 (2)  | O3—P3         | 1.503 (2)   |
| Fe—N1            | 2.024 (2)  | N1—C1         | 1.165 (3)   |
| Fe—O1            | 2.036 (2)  | C1—S1         | 1.616 (2)   |
| Fe—N2            | 2.039 (2)  | N2—C2         | 1.166 (3)   |
| Fe—N3            | 2.045 (2)  | C2—S2         | 1.628 (2)   |
| O1—P1            | 1.509 (12) | N3—C3         | 1.170 (3)   |
| O1—P11           | 1.53 (2)   | C3—S3         | 1.624 (2)   |
| O2—Fe—O3         | 90.27 (6)  | N1—Fe—N3      | 179.00 (7)  |
| O2—Fe—N1         | 90.09 (7)  | O1—Fe—N3      | 90.96 (7)   |
| O3—Fe—N1         | 88.96 (7)  | N2—Fe—N3      | 89.73 (7)   |
| O2—Fe—O1         | 86.45 (6)  | P1—O1—Fe      | 137.9 (5)   |
| O3—Fe—O1         | 176.55 (6) | P11—O1—Fe     | 137.0 (10)  |
| N1—Fe—O1         | 89.97 (7)  | P2—O2—Fe      | 166.29 (10) |
| O2—Fe—N2         | 177.10 (7) | P3—O3—Fe      | 171.21 (10) |
| O3—Fe—N2         | 92.63 (7)  | N1—C1—S1      | 179.2 (2)   |
| N1—Fe—N2         | 89.90 (7)  | C2—N2—Fe      | 170.78 (17) |
| O1—Fe—N2         | 90.65 (7)  | N2—C2—S2      | 179.03 (19) |
| O2—Fe—N3         | 90.33 (7)  | C3—N3—Fe      | 177.56 (17) |
| O3—Fe—N3         | 90.13 (7)  | N3—C3—S3      | 179.1 (2)   |
| O1—P1—C13—C23    | −66.4 (13) | O2—P2—C16—C26 | −63.1 (2)   |
| O1—P11—C131—C231 | −63 (3)    | O3—P3—C19—C29 | −61.22 (10) |



**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The H atoms and the minor disorder component have been omitted for clarity.

**Table 2**

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                              | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---|-------|--------------|--------------|----------------|
| C131—H134 <sup>i</sup> ···S2 <sup>i</sup>   | 0.99  | 2.77         | 3.64 (3)     | 146            |
| C321—H321 <sup>i</sup> ···S3 <sup>i</sup>   | 0.95  | 2.73         | 3.632 (12)   | 158            |
| C19—H192 <sup>ii</sup> ···S3 <sup>ii</sup>  | 0.99  | 2.86         | 3.848 (2)    | 177            |
| C47—H47 <sup>iii</sup> ···S2 <sup>iii</sup> | 0.95  | 2.83         | 3.707 (2)    | 154            |
| C16—H162 <sup>iv</sup> ···S2 <sup>iv</sup>  | 0.99  | 2.80         | 3.754 (2)    | 163            |

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + 2, -y + 1, -z + 1$ ; (iii)  $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iv)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ .

The C atoms of one phenyl group attached to atom P1 of the ethyldiphenylphosphine oxide ligand exhibited extremely prolate displacement ellipsoids, and the displacement parameters of atom P1 and the C atoms of the ethyl substituent were larger than those of the two other ligands. This apparent disorder was modelled by splitting the phenyl (C12–C62) and ethyl (C13, C23) groups and atom P1 over two sets of positions, giving refined occupancies of 0.653 (12) for one component and 0.337 (12) for the other component (atoms C121–C621, C131, C231 and P11). The disordered groups were refined with geometrical similarity restraints (Sheldrick, 1997). The anisotropic displacement parameters of the atom pairs from the two components were constrained to be identical. Finally,  $U^{ij}$  parameters for C12 and C121 were restrained to approximate an isotropic behaviour. H atoms were positioned geometrically and treated as riding on their carrier atom, with C–H distances constrained to 0.95 (aromatic CH), 0.99 (methylene CH<sub>2</sub>) or 0.98 Å (methyl CH<sub>3</sub>), and with  $U_{\text{iso}}(\text{H})$  values equal to  $1.5U_{\text{eq}}(\text{carrier C})$  for methyl groups and  $1.2U_{\text{eq}}(\text{carrier C})$  for the remaining H atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

## References

- Bruker (1998). *XP*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* **A51**, 887–897.
- Olejník, Z., Lis, T. & Ondrejčovičová, I. (1995). *Acta Cryst.* **C51**, 2246–2249.
- Oxford Diffraction (2003). *KM-4 CCD Software*, including *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171. Oxford Diffraction Poland, Wrocław, Poland.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.