

Synthesis, crystal structure and DFT study of carbonyl[3-(dibenzo[*b,d*]thiophen-4-yl)-6-(pyridin-2-yl- κN)pyridazine- κN^1]bis(trimethylphosphane)-iron(0)

Ryota Futaki, Noriko Chikaraishi Kasuga and Masakazu Hirotsu*

Department of Chemistry, Faculty of Science, Kanagawa University, Kanagawa-ku, Yokohama 221-8686, Japan.

*Correspondence e-mail: mhiro@kanagawa-u.ac.jp

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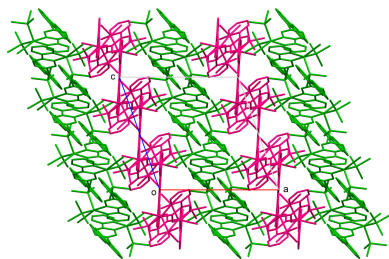
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The title compound, $[\text{Fe}(\text{C}_{21}\text{H}_{13}\text{N}_3\text{S})(\text{CO})(\text{PMe}_3)_2]$ (**2**), bearing a 3-(dibenzo[*b,d*]thiophen-4-yl)-6-(pyridin-2-yl)pyridazine ligand was obtained by the reaction of $[\text{Fe}(\text{C}_{21}\text{H}_{13}\text{N}_3\text{S})(\text{CO})_3]$ (**1**) with $[\text{Fe}(\text{PMe}_3)_4]$. Crystal structure analysis of **2** revealed that the *N,N*-bidentate and three monodentate ligands form a five-coordinate square-pyramidal geometry around Fe, which differs from the trigonal-bipyramidal geometry observed in **1**. The steric and electronic factors were investigated by combining crystal structure and density functional theory (DFT) calculations. Compared with CO, the better σ donor properties of PMe_3 induce the square-pyramidal geometry of **2**, and a significant π -back-bonding interaction was confirmed between Fe and the pyridazine moiety.

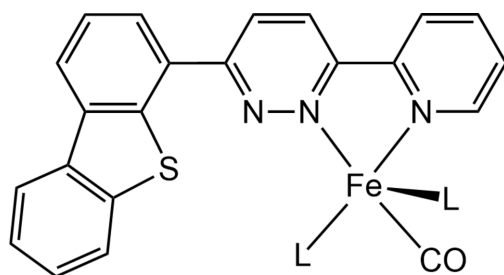
1. Chemical context

The utilization of earth-abundant transition-metal catalysts has become increasingly important, and iron-catalyzed reactions are attractive research topics (Bolm *et al.*, 2004; Bauer & Knölker, 2015; Takeda *et al.*, 2017; Ekspong *et al.*, 2021; Gao *et al.*, 2022; Sila *et al.*, 2024). Low-valent iron complexes have been studied intensively because their unsaturated coordination sites are highly active and play a pivotal role in catalytic reactions (Toya *et al.*, 2017; Takeshita *et al.*, 2018; Nakajima *et al.*, 2025; Zhang *et al.*, 2025; Wang *et al.*, 2025). Iron carbonyls are attractive catalysts and precatalysts for fundamental organic and inorganic reactions (Schroeder & Wrighton, 1976; Petricci *et al.*, 2018; Hirayama *et al.*, 2025; Torrent *et al.*, 2000). For example, $[\text{Fe}(\text{CO})_5]$ catalyzes the water–gas shift reaction and isomerization of olefins (Schroeder & Wrighton, 1976), and $[\text{Fe}_2(\text{CO})_9]$ and $[\text{Fe}_3(\text{CO})_{12}]$ are catalyst precursors for the reductive amination of aldehydes (Petricci *et al.*, 2018; Hirayama *et al.*, 2025). Furthermore, various diiron carbonyl complexes with thiolate ligands have been synthesized from $[\text{Fe}(\text{CO})_5]$ and are promising candidates for the active-site model of $[\text{FeFe}]$ -hydrogenases (Tard & Pickett, 2009).

We previously reported diiron hydrogenase mimics bearing thiolate ligands, which were synthesized by the photoreactions of $[\text{Fe}(\text{CO})_5]$ with dibenzothiophene derivatives containing Schiff base or pyridine moieties *via* C–S bond cleavage (Hirotsu *et al.*, 2012, 2014; Nakae *et al.*, 2015). However, the corresponding reaction with 3-(dibenzo[*b,d*]thiophen-4-yl)-6-(pyridin-2-yl)pyridazine (dbtpdzpy) gave the iron(0) carbonyl complex $[\text{Fe}(\text{dbtpdzpy})(\text{CO})_3]$ (**1**), in which the dbtpdzpy ligand is bound to Fe in an *N,N*-bidentate fashion, forming a five-membered chelate ring (Futaki *et al.*, 2025). We carried out the reaction of **1** with the reactive iron(0) complex



[Fe(PMe₃)₄] in THF, expecting the remaining N atom to act as a directing group for C—S bond activation. However, the N,S-coordination site remained intact, and the five-coordinate iron(0) complex [Fe(dbtpdzpy)(CO)(PMe₃)₂] (**2**) was obtained, in which the two carbonyl ligands in **1** are replaced by PMe₃ dissociated from [Fe(PMe₃)₄]. The reaction of **1** with PMe₃ gives dbtpdzpy and carbonyl trimethylphosphane iron(0) complexes such as [Fe(CO)₃(PMe₃)₂]; therefore, this ligand scrambling reaction provides a suitable route for the preparation of **2**. The crystal structure of the bis(trimethylphosphane) iron(0) complex **2** showed geometrical changes around the Fe from **1**, including a significant shortening of the Fe—N(pyridazine) bonds, which is discussed in terms of the steric and electronic effects of PMe₃.



1: L = CO
2: L = PMe₃

2. Structural commentary

Complex **2** crystallizes in the centrosymmetric space group *P*2₁/*c* (No. 14) with two independent [Fe(dbtpdzpy)(CO)(PMe₃)₂] molecules, 2A and 2B, in the asymmetric unit (Fig. 1). Selected bond distances and angles are listed in Table 1. The five-coordinate iron center is chelated by the *N,N*-bidentate ligand dbtpdzpy, and the carbonyl ligand is located *trans* to the pyridazine N atom. The remaining sites are occupied by two PMe₃ ligands, and the dibenzo[*b,d*]thiophen-4-yl group is oriented away from the PMe₃ ligands. This contrasts with the near planar arrangement of the aromatic rings observed in **1**. Both molecules 2A and 2B have a distorted square-pyramidal coordination geometry, and one of the two PMe₃ ligands occupies the apical position of the pyramid. The structural index parameter τ is 0.18 for 2A and 0.023 for 2B, suggesting a larger distortion of 2A from the ideal square-pyramidal geometry (Addison *et al.*, 1984). The differences are visualized by overlaying the molecular structures of 2A and 2B (symmetry operation: $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$), where the central pyridazine ring is superposed (Fig. 2). Significant differences were detected in the two N(pyridine)—Fe—P angles and the interplanar angles between the dibenzothiophene/pyridazine/pyridine moieties.

In the crystal structure of **2**, the two PMe₃ ligands occupy the less crowded apical and basal positions. The stronger σ donor properties of PMe₃ relative to CO make the Fe center of **2** more electron-rich than that of **1**. This affects the bond lengths around Fe due to enhanced π -back-bonding inter-

Table 1

Selected geometric parameters (Å, °).

Fe1—P1	2.2144 (4)	Fe2—P3	2.2087 (4)
Fe1—P2	2.1847 (5)	Fe2—P4	2.1862 (4)
Fe1—N2	1.9054 (12)	Fe2—N5	1.9117 (12)
Fe1—N3	1.9464 (13)	Fe2—N6	1.9434 (13)
Fe1—C22	1.7426 (17)	Fe2—C50	1.7371 (16)
H9...C17 ⁱ	2.676	H23C...C34 ⁱⁱⁱ	2.824
H15...C34 ⁱⁱ	2.704	H25C...C52 ^v	2.834
H2...C43 ⁱⁱ	2.730	H49 ^{vi} ...H32 ⁱⁱⁱ	2.336
C8...H53B ⁱⁱⁱ	2.755	C6...H30	2.841
H15...C36 ⁱⁱ	2.770	H23B...S2 ⁱⁱⁱ	2.943
S1...C42 ⁱⁱ	3.389	H5...C19 ⁱ	2.843
O2...H48 ^{iv}	2.616	H19...O2 ^{iv}	2.664
H18...C32 ⁱⁱ	2.798		
P2—Fe1—P1	99.457 (18)	P4—Fe2—P3	98.499 (17)
N2—Fe1—P1	91.04 (4)	N5—Fe2—P3	94.01 (4)
N2—Fe1—P2	102.65 (4)	N5—Fe2—P4	102.48 (4)
N3—Fe1—P1	153.19 (4)	N6—Fe2—P3	163.19 (4)
C22—Fe1—N2	163.93 (7)	C50—Fe2—N5	161.83 (6)

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

actions. The Fe—C(carbonyl) bond lengths of **2** [1.7426 (17), 1.7371 (16) Å] are shorter than those of **1** [1.771 (2), 1.801 (2), 1.7774 (18) Å]. This is consistent with a large red shift of the CO stretching frequency for **2** (1844 cm⁻¹) compared to **1** (1984 cm⁻¹, 1925 cm⁻¹, 1894 cm⁻¹). Furthermore, the Fe—N(pyridazine) bond lengths of **2** [1.9054 (12), 1.9117 (12) Å] are approximately 0.04 Å shorter than that of **1**

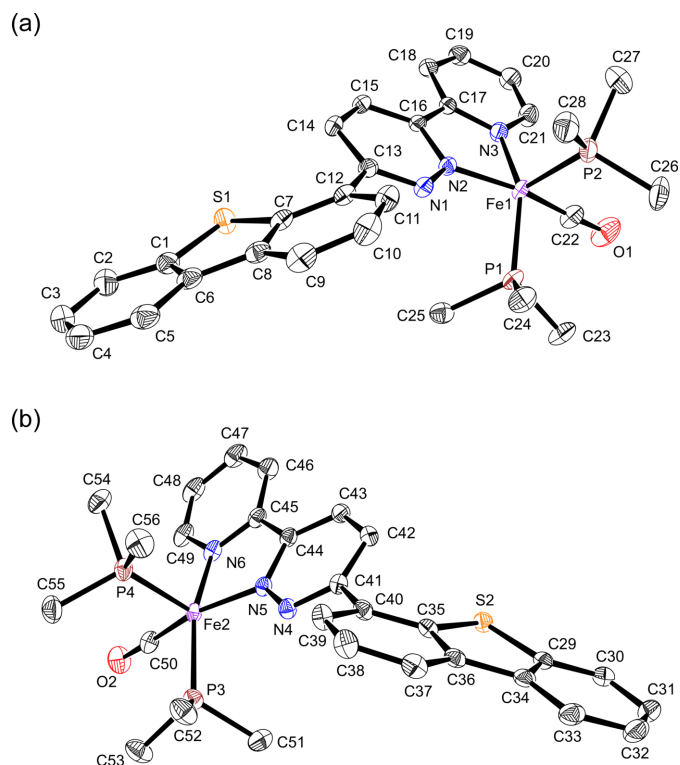


Figure 1

Perspective view of molecules (a) 2A and (b) 2B in **2** with displacement ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2Structural indices (τ) and geometric parameters ($\text{\AA}$, $^\circ$) for experimental (**1**, 2A in **2**, 2B in **2**) and computational (**2**, **3**, **4**, **5**) results.

	1 ^a	2A ^b	2B ^b	2 ^c	3 ^c	4 ^c	5 ^c
τ	0.649	0.179	0.023	0.017	0.045	0.293	0.759
Fe–N(pyridazine)	1.9487 (14)	1.9054 (12)	1.9117 (12)	1.914	1.909	1.892	1.927
Fe–N(pyridine)	1.9622 (14)	1.9464 (13)	1.9434 (13)	1.971	1.971	1.966	1.987
N–Fe–N	80.27 (6)	80.70 (5)	80.86 (5)	80.75	80.65	80.86	80.31
Interplanar angle ^d	3.94 (7)	46.79 (4)	52.56 (4)	55.79	–	–	–
Interplanar angle ^e	4.02 (9)	3.03 (8)	9.63 (8)	0.57	1.18	0.35	0

Notes: (a) Futaki *et al.* (2025); (b) experimental data; (c) data from DFT calculations; (d) interplanar angles were calculated as the dihedral angle between the least-squares planes of the dibenzothiophene and pyridazine moieties; (e) interplanar angles were calculated as the dihedral angle between the least-squares planes of the pyridazine and pyridine moieties.

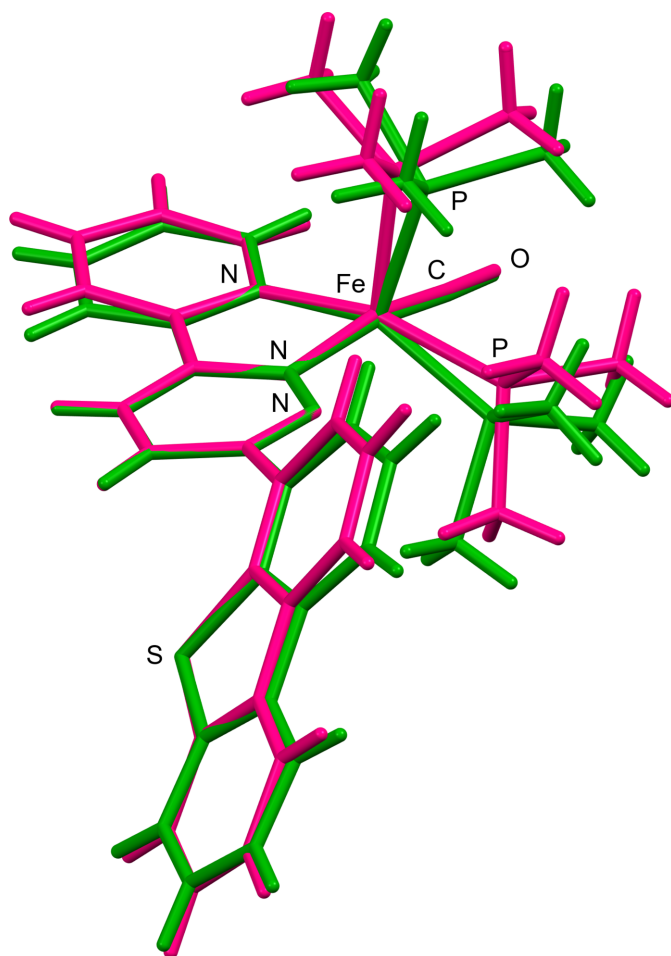
[1.9487 (14) $\text{\AA}$], whereas the N–N(coordinated) [1.3736 (17), 1.3826 (16) $\text{\AA}$] and N(coordinated)–C [1.3954 (18), 1.3964 (18) $\text{\AA}$] bond lengths in the pyridazine ring of **2** are longer than those of **1** [N–N(coordinated), 1.3600 (18) $\text{\AA}$; N(coordinated)–C, 1.363 (2) $\text{\AA}$], respectively. These findings are consistent with the moderate π acceptor character of pyridazine.

3. Density functional theory calculations

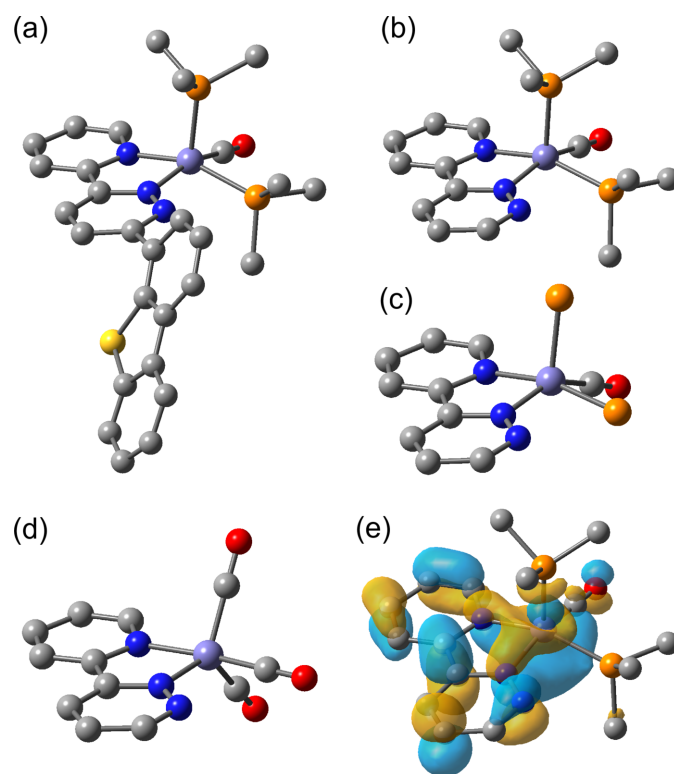
To analyze τ value differences, the structures of **2** and related complexes were optimized by density functional theory (DFT) calculations at the B3LYP/6-311+G(d,p) level. All DFT

calculations in this study were carried out using the *Gaussian 16* program (Frisch *et al.*, 2016), and the results were visualized using the *GaussView 6.0* software (Dennington *et al.*, 2016). The resulting structural indices τ and selected geometric parameters are summarized in Table 2. The crystal structures of 2A and 2B were used as the initial models for the calculations, which yielded identical results (Fig. 3a). The τ value of 0.017 for the optimized structure is close to that of 2B. To exclude the influence of the dibenzothiophene moiety, the structure of [Fe(pypdz)(CO)(PMe₃)₂] (**3**) (pypdz = 3-(pyridin-2-yl)pyridazine) was also optimized (Fig. 3b), and a τ value of 0.045 was obtained. These results suggest that the geometry around the Fe atom of 2A is more strongly influenced by the crystal packing effects, as mentioned later.

The square-pyramidal geometry of **2** differs from the trigonal-bipyramidal geometry of **1** ($\tau = 0.65$). The pyridazine moiety in **1** occupies an equatorial position, which is likely due

**Figure 2**

Overlay of molecules 2A (green, symmetry operation: x, y, z) and 2B (magenta, symmetry operation: $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$).

**Figure 3**

Optimized structures of (a) **2**, (b) [Fe(pypdz)(CO)(PMe₃)₂] (**3**), (c) [Fe(pypdz)(CO)(PH₃)₂] (**4**), and (d) [Fe(pypdz)(CO)₃] (**5**). (e) HOMO of **3** (isovalue = 0.03 Bohr^{-3/2}). Hydrogen atoms are omitted for clarity.

to its better π acceptor properties than those of pyridine. The bite angles of the *N,N*-chelate in **2A** [80.70 (5)°] and **2B** [80.86 (5)°] are comparable to that in **1** [80.27 (6)°]. To conform the preference for the square-pyramidal geometry in **2** while excluding the packing and substituent effects, the structure of the analogous iron complex with the less bulky PH_3 ligands, $[\text{Fe}(\text{pypdz})(\text{CO})(\text{PH}_3)_2]$ (**4**), was optimized by DFT calculations (Fig. 3c). The τ value of 0.29 suggests that complex **4** has a distorted square-pyramidal geometry. Furthermore, the optimized structure of $[\text{Fe}(\text{pypdz})(\text{CO})_3]$ (**5**) (Fig. 3d, $\tau = 0.76$) is similar to that of the bipyridine complex $[\text{Fe}(\text{bpy})(\text{CO})_3]$ (bpy = 2,2'-bipyridine) with a trigonal-bipyramidal geometry: $\tau = 0.83$ (Calderazzo *et al.*, 2002), 0.81 (DelaVarga *et al.*, 2003). Therefore, the geometrical change between **1** and **2** is mainly attributable to the electronic effect of the PMe_3 ligand, which is a better σ -donor and poorer π -acceptor ligand than CO. Fig. 3e shows the HOMO of the bis(trimethylphosphane) complex **2**, which is located over the pypdz ligand and the iron center. This molecular orbital is a combination of the metal d orbital and the LUMO of pypdz, showing the π -back-donation from Fe to pypdz. Natural population analysis of **3** (natural charge (*e*): Fe, −1.145; pyridine, −0.042; pyridazine, −0.241) and **5** (natural charge (*e*): Fe, −1.240; pyridine, 0.165; pyridazine, 0.016) also revealed that the pyridazine moiety in the PMe_3 complex **3** effectively accepts electron density from Fe: the difference in natural charge between **3** and **5** is 0.207*e* in the pyridine moiety and 0.257*e* in the pyridazine moiety.

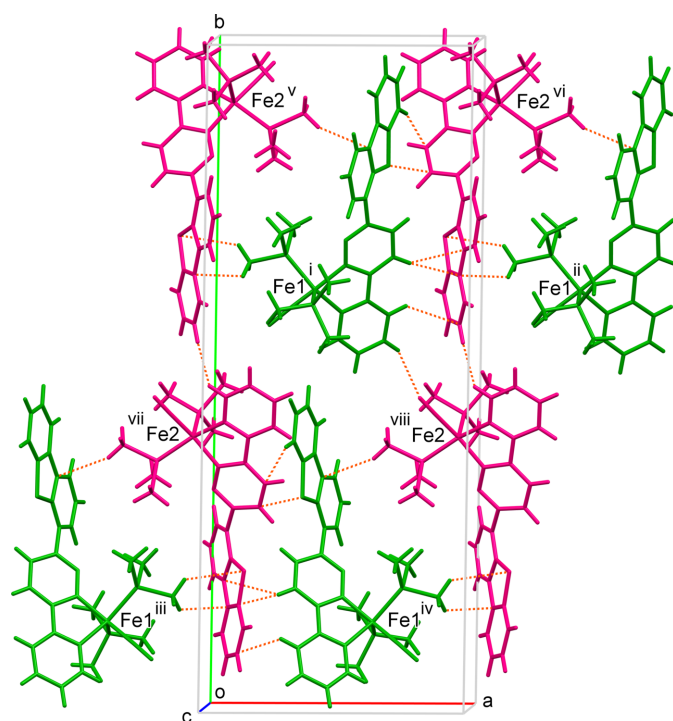


Figure 4
Partial view of the crystal packing of **2**, showing a pair of **2A** (green) and **2B** (magenta) molecules. Short contacts are shown as dashed lines. [Symmetry codes: (i) x, y, z ; (ii) $x + 1, y, z$; (iii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$; (vi) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (vii) $-x + 1, -y + 1, -z + 1$; (viii) $-x + 2, -y + 1, -z + 1$.]

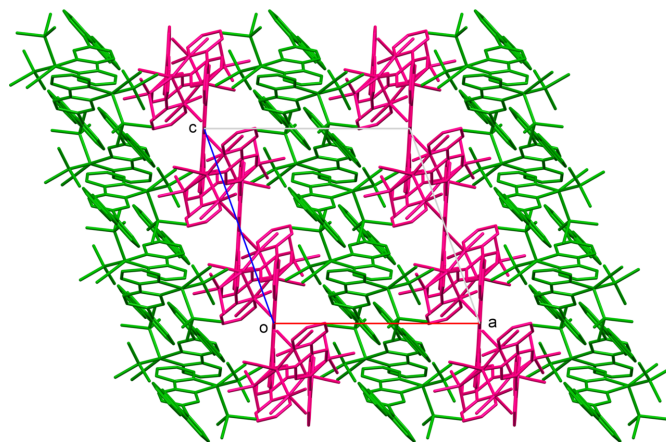


Figure 5
Crystal packing diagram of **2** along the *b* axis, showing the layers of **2A** (green) and **2B** (magenta).

4. Supramolecular features

Molecules **2A** (symmetry operation: x, y, z) and **2B** (symmetry operation: $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$) are related by a pseudo C_2 axis along the *c* axis in the crystal, and four pairs located on the *ab* plane are shown in Fig. 4. The PMe_3 ligand at the basal position is located near the dibenzothiophene moiety of the paired molecule. The basal PMe_3 ligands are fitted into a cavity consisting of aromatic ligands. Some short contacts are found between **2A** and **2B**, mainly along the *a* axis, which are

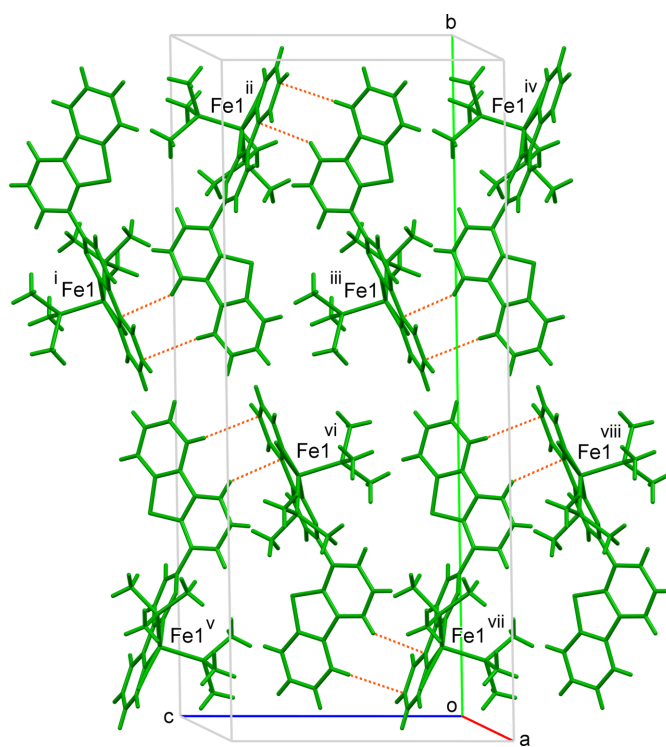


Figure 6
Partial view of the crystal packing of **2**, showing the layers of **2A**. Short contacts are shown as dashed lines. [Symmetry codes: (i) $x, y, z + 1$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) x, y, z ; (iv) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (v) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x + 1, -y + 1, -z + 1$; (vii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (viii) $-x + 1, -y + 1, -z$.]

attributed to C—H... π interactions: *e.g.*, H15...C34($x, -y + \frac{3}{2}, z - \frac{1}{2}$), H2...C43($x, -y + \frac{3}{2}, z - \frac{1}{2}$), C8...C53B($x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$) (Table 1).

Fig. 5 shows the crystal packing of **2** along the *b* axis. The layers of 2A and 2B are parallel to the *bc* plane and stacked alternately along the *a* axis. As shown in Fig. 6, short contacts due to C—H... π interactions are observed only in the 2A layer: H9...C17($x, -y + \frac{3}{2}, z + \frac{1}{2}$), H5...C19($x, -y + \frac{3}{2}, z + \frac{1}{2}$) (Table 1). The crystal packing affects the interplanar angles of the dibenzothiophene and pyridazine moieties of 2A. This induces a deviation in the N(pyridine)—Fe—P angles through steric interactions. Therefore, 2A is more distorted from the ideal square-pyramidal geometry than 2B.

5. Database survey

Various transition-metal complexes containing a pyridyl-pyridazine unit in the ligands have been structurally characterized by X-ray crystallography: Fe (Futaki *et al.*, 2025; Guo *et al.*, 2021), Ru (De Munno *et al.*, 1988; Xu *et al.*, 2009), Pt (McCready & Puddephatt, 2015), Co, Ni, Zn (Savjani *et al.*, 2015), Re (Sangilipandi *et al.*, 2015; Mosberger *et al.*, 2019; Schnierle *et al.*, 2022). However, structural reports on iron complexes are rare (Futaki *et al.*, 2025; Guo *et al.*, 2021).

6. Synthesis and crystallization

A suspension of complex **1** (0.058 g, 0.12 mmol) and [Fe(PMe₃)₄] (0.016 g, 0.11 mmol) in tetrahydrofuran (THF) (10 mL) was stirred at room temperature under a nitrogen atmosphere for 1 d. The resulting deep brown solution was concentrated to dryness under reduced pressure to afford a red-brown solid. The solid was dissolved in toluene, and hexane was layered on top of the solution. The mixture was cooled to 253 K, and the precipitated red-brown solid was removed by decantation. The resulting blue-green solution was stored at 253 K to yield **2** as red-brown crystals (3.6 mg, 5%). The low yield is probably due to the high solubility of **2** in toluene and hexane. ¹H NMR (600 MHz, C₆D₆): δ 9.83 (*d*, *J* = 6.2 Hz, 1H), 7.94 (*m*, 2H), 7.89 (*d*, *J* = 8.0 Hz, 1H), 7.55 (*dd*, *J* = 8.0, 0.4 Hz, 1H), 7.44 (*td*, *J* = 7.6, 0.4 Hz, 1H), 7.32 (*m*, 1H), 7.26 (*dd*, *J* = 8.6, 0.4 Hz, 1H), 7.21 (*m*, 1H), 7.15 (*m*, 1H), 6.97 (*td*, *J* = 8.6, 1.4 Hz, 1H), 6.80 (*m*, 1H), 6.52 (*td*, *J* = 6.6, 1.0 Hz, 1H), 1.05 (*d*, *J* = 7.6 Hz, 18H). ³¹P{¹H} NMR (243 MHz, C₆D₆): δ 22.7. ν_{CO} /cm^{−1} (KBr): 1844. Analysis calculated for C₂₈H₃₁FeN₃OP₂S·0.9H₂O: C, 56.84, H, 5.59, N, 7.10. Found: C, 56.52; H, 5.27; N, 7.59.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with C—H(aromatic) = 0.95 Å and C—H(methyl) = 0.98 Å, and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{C})$, respectively.

Table 3
Experimental details.

Crystal data	
Chemical formula	[Fe(C ₂₁ H ₁₃ N ₃ S)(C ₃ H ₉ P) ₂ (CO)]
<i>M_r</i>	575.41
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	90
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.4551 (3), 32.3786 (7), 13.5356 (3)
β (°)	109.700 (3)
<i>V</i> (Å ³)	5551.7 (2)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	0.76
Crystal size (mm)	0.24 × 0.21 × 0.08
Data collection	
Diffractometer	ROD, Synergy Custom system, HyPix
Absorption correction	Multi-scan (CrysAlis PRO; Rigaku OD, 2024)
<i>T</i> _{min} , <i>T</i> _{max}	0.878, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	62645, 14433, 12163
<i>R</i> _{int}	0.033
(<i>sin</i> θ / λ) _{max} (Å ^{−1})	0.725
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.083, 1.04
No. of reflections	14433
No. of parameters	661
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.52, −0.39

Computer programs: CrysAlis PRO (Rigaku OD, 2024), SHELXT2018/2 (Sheldrick, 2015a), SHELXL2019/3 (Sheldrick, 2015b) and OLEX2 (Dolomanov *et al.*, 2009).

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References

- Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Bauer, I. & Knölker, H.-J. (2015). *Chem. Rev.* **115**, 3170–3387.
- Bolm, C., Legros, J., Le Paih, J. & Zani, L. (2004). *Chem. Rev.* **104**, 6217–6254.
- Calderazzo, F., Falaschi, S., Marchetti, F. & Pampaloni, G. (2002). *J. Organomet. Chem.* **662**, 137–143.
- DelaVarga, M., Costa, R., Reina, R., Núñez, A., Ángel Maestro, M. & Mah'f'ia, J. (2003). *J. Organomet. Chem.* **677**, 101–117.
- De Munno, G., Denti, G., De Rosa, G. & Bruno, G. (1988). *Acta Cryst.* **C44**, 1193–1196.
- Dennington, R., Keith, T. A. & Millam, J. M. (2016). *GaussView 6.0.16* Semichem Inc., Shawnee Mission, KS, USA.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Ekspong, J., Larsen, C., Stenberg, J., Kwong, W. L., Wang, J., Zhang, J., Johansson, E. M. J., Messinger, J., Edman, L. & Wågberg, T. (2021). *ACS Sustainable Chem. Eng.* **9**, 14070–14078.
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A. V., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R.,

- Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery, J. A., Peralta, J. E. Jr, Ogliaro, F., Bearpark, M. J., Heyd, J. J., Brothers, E. N., Kudin, K. N., Staroverov, V. N., Keith, T. A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A. P., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B. & Fox, D. J. (2016). *Gaussian 16* Revision C. 01. Gaussian, Inc., Wallingford CT, USA.
- Futaki, R., Chikaraishi Kasuga, N. & Hirotsu, M. (2025). *Inorg. Chem.* **64**, 23225–23237.
- Gao, Y., Pink, M., Carta, V. & Smith, J. M. (2022). *J. Am. Chem. Soc.* **144**, 17165–17172.
- Guo, Z., You, M., Deng, Y.-F., Liu, Q., Meng, Y.-S., Pikramenou, Z. & Zhang, Y.-Z. (2021). *Dalton Trans.* **50**, 14303–14308.
- Hirayama, Y., Miura, A., Hirayama, M., Nakamura, H., Fujita, K., Kageyama, H., Yamaguchi, S., Mizugaki, T. & Mitsudome, T. (2025). *Small* **21**, 2412217.
- Hirotsu, M., Santo, K., Hashimoto, H. & Kinoshita, I. (2012). *Organometallics* **31**, 7548–7557.
- Hirotsu, M., Santo, K., Tsuboi, C. & Kinoshita, I. (2014). *Organometallics* **33**, 4260–4268.
- McCready, M. S. & Puddephatt, R. J. (2015). *Organometallics* **34**, 2261–2270.
- Mosberger, M., Probst, B., Spingler, B. & Alberto, R. (2019). *Eur. J. Inorg. Chem.* pp. 3518–3525.
- Nakae, T., Hirotsu, M. & Kinoshita, I. (2015). *Organometallics* **34**, 3988–3997.
- Nakajima, Y., Iizuka, K., Takeshita, T., Fujimori, S., Shimoyama, Y., Sato, K., Yoshida, M., Ni, S.-F. & Sakaki, S. (2025). *JACS Au* **5**, 2033–2039.
- Petricci, E., Santillo, N., Castagnolo, D., Cini, E. & Taddei, M. (2018). *Adv. Synth. Catal.* **360**, 2560–2565.
- Rigaku OD (2024). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
- Sangilipandi, S., Nagarajaprakash, R., Sutradhar, D., Kaminsky, W., Chandra, A. K. & Mohan Rao, K. (2015). *Inorg. Chim. Acta* **437**, 177–187.
- Savjani, N., Singh, K. & Solan, G. A. (2015). *Inorg. Chim. Acta* **436**, 184–194.
- Schnierle, M., Winkler, M., Filippou, V., van Slageren, J. & Ringenberg, M. R. (2022). *Eur. J. Inorg. Chem.* pp. e202100998.
- Schroeder, M. A. & Wrighton, M. S. (1976). *J. Am. Chem. Soc.* **98**, 551–558.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Sila, N., Dürrmann, A., Weber, B., Heinemann, F. W., Irrgang, T. & Kempe, R. (2024). *J. Am. Chem. Soc.* **146**, 26877–26883.
- Takeda, H., Cometto, C., Ishitani, O. & Robert, M. (2017). *ACS Catal.* **7**, 70–88.
- Takeshita, T., Sato, K. & Nakajima, Y. (2018). *Dalton Trans.* **47**, 17004–17010.
- Tard, C. & Pickett, C. J. (2009). *Chem. Rev.* **109**, 2245–2274.
- Torrent, M., Solà, M. & Frenking, G. (2000). *Chem. Rev.* **100**, 439–494.
- Toya, Y., Hayasaka, K. & Nakazawa, H. (2017). *Organometallics* **36**, 1727–1735.
- Wang, J., Bai, H., Xi, X., He, R., Dong, X., Ju, G. & Wang, C. (2025). *J. Am. Chem. Soc.* **147**, 29666–29672.
- Xu, Y., Åkermark, T., Gyollai, V., Zou, D., Eriksson, L., Duan, L., Zhang, R., Åkermark, B. & Sun, L. (2009). *Inorg. Chem.* **48**, 2717–2719.
- Zhang, Z.-J., Golling, S., Cattani, S., Chen, X. & Ackermann, L. (2025). *J. Am. Chem. Soc.* **147**, 6897–6904.

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Synthesis, crystal structure and DFT study of carbonyl[3-(dibenzo[*b,d*]thiophen-4-yl)-6-(pyridin-2-yl- κ N)pyridazine- κ N¹]bis(trimethylphosphane)iron(0)

Ryota Futaki, Noriko Chikaraishi Kasuga and Masakazu Hirotsu

Computing details

Carbonyl[3-(dibenzo[*b,d*]thiophen-4-yl)-6-(pyridin-2-yl- κ N)pyridazine- κ N¹]bis(trimethylphosphane)iron(0)

Crystal data

[Fe(C₂₁H₁₃N₃S)(C₃H₉P)₂(CO)]

$M_r = 575.41$

Monoclinic, $P2_1/c$

$a = 13.4551$ (3) Å

$b = 32.3786$ (7) Å

$c = 13.5356$ (3) Å

$\beta = 109.700$ (3)°

$V = 5551.7$ (2) Å³

$Z = 8$

$F(000) = 2400$

$D_x = 1.377$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 32963 reflections

$\theta = 3.0$ – 31.0 °

$\mu = 0.76$ mm⁻¹

$T = 90$ K

Block, dark red

$0.24 \times 0.21 \times 0.08$ mm

Data collection

ROD, Synergy Custom system, HyPix
diffractometer

Radiation source: Rotating-anode X-ray tube,
Rigaku (Mo) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2024)

$T_{\min} = 0.878$, $T_{\max} = 1.000$

62645 measured reflections

14433 independent reflections

12163 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 31.0$ °, $\theta_{\min} = 3.0$ °

$h = -17 \rightarrow 18$

$k = -43 \rightarrow 45$

$l = -19 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.083$

$S = 1.04$

14433 reflections

661 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 2.4796P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.52$ e Å⁻³

$\Delta\rho_{\min} = -0.38$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.38565 (2)	0.62411 (2)	0.32029 (2)	0.01969 (5)
S1	0.65732 (3)	0.81061 (2)	0.34172 (3)	0.02582 (8)
P1	0.27314 (3)	0.67629 (2)	0.29259 (3)	0.02223 (8)
P2	0.38516 (3)	0.60425 (2)	0.47438 (3)	0.02675 (9)
O1	0.21163 (11)	0.56935 (5)	0.21116 (13)	0.0481 (4)
N1	0.50321 (9)	0.69917 (4)	0.40088 (10)	0.0198 (2)
N2	0.50212 (9)	0.66130 (4)	0.35479 (10)	0.0183 (2)
N3	0.48680 (10)	0.58951 (4)	0.28443 (10)	0.0217 (3)
C1	0.65719 (12)	0.86409 (5)	0.36221 (13)	0.0246 (3)
C2	0.69065 (14)	0.89446 (5)	0.30716 (15)	0.0330 (4)
H2	0.717215	0.887173	0.252789	0.040*
C3	0.68421 (14)	0.93547 (6)	0.33368 (17)	0.0368 (4)
H3	0.705747	0.956544	0.296416	0.044*
C4	0.64648 (13)	0.94620 (5)	0.41441 (16)	0.0341 (4)
H4	0.643307	0.974455	0.432018	0.041*
C5	0.61366 (13)	0.91610 (5)	0.46902 (14)	0.0298 (4)
H5	0.587732	0.923626	0.523684	0.036*
C6	0.61888 (12)	0.87442 (5)	0.44327 (13)	0.0239 (3)
C7	0.60539 (11)	0.80132 (5)	0.44243 (12)	0.0206 (3)
C8	0.58965 (11)	0.83825 (5)	0.49030 (12)	0.0223 (3)
C9	0.54778 (13)	0.83641 (5)	0.57167 (13)	0.0285 (3)
H9	0.536400	0.861084	0.604326	0.034*
C10	0.52310 (14)	0.79876 (6)	0.60427 (13)	0.0306 (4)
H10	0.496256	0.797487	0.660745	0.037*
C11	0.53711 (12)	0.76234 (5)	0.55518 (12)	0.0256 (3)
H11	0.518623	0.736683	0.578313	0.031*
C12	0.57760 (11)	0.76281 (5)	0.47301 (11)	0.0205 (3)
C13	0.58684 (11)	0.72335 (4)	0.42035 (11)	0.0192 (3)
C14	0.67901 (11)	0.71251 (5)	0.39751 (12)	0.0221 (3)
H14	0.736322	0.731176	0.409316	0.026*
C15	0.68116 (11)	0.67382 (5)	0.35766 (12)	0.0216 (3)
H15	0.742054	0.664646	0.343480	0.026*
C16	0.59346 (11)	0.64774 (4)	0.33777 (11)	0.0180 (3)
C17	0.58394 (11)	0.60719 (5)	0.29734 (11)	0.0194 (3)
C18	0.66233 (12)	0.58596 (5)	0.26952 (13)	0.0239 (3)
H18	0.727201	0.599297	0.276343	0.029*
C19	0.64543 (13)	0.54640 (5)	0.23288 (13)	0.0277 (3)
H19	0.697584	0.532025	0.213456	0.033*
C20	0.54883 (14)	0.52740 (5)	0.22459 (14)	0.0302 (3)

H20	0.535820	0.499579	0.201572	0.036*
C21	0.47386 (13)	0.54929 (5)	0.24990 (14)	0.0290 (3)
H21	0.409064	0.535920	0.243231	0.035*
C22	0.28045 (13)	0.59203 (5)	0.25351 (15)	0.0304 (4)
C23	0.13493 (13)	0.66352 (6)	0.22311 (16)	0.0362 (4)
H23A	0.127604	0.652293	0.153767	0.054*
H23B	0.091754	0.688497	0.214917	0.054*
H23C	0.111248	0.642914	0.263357	0.054*
C24	0.25876 (14)	0.70886 (6)	0.39819 (14)	0.0318 (4)
H24A	0.235197	0.691853	0.445979	0.048*
H24B	0.206543	0.730532	0.367829	0.048*
H24C	0.326873	0.721546	0.437045	0.048*
C25	0.29402 (13)	0.71554 (5)	0.20477 (13)	0.0277 (3)
H25A	0.360776	0.729905	0.239720	0.042*
H25B	0.235789	0.735455	0.186881	0.042*
H25C	0.296706	0.702333	0.140576	0.042*
C26	0.25739 (16)	0.59587 (7)	0.49069 (17)	0.0423 (5)
H26A	0.218956	0.622090	0.481403	0.063*
H26B	0.268261	0.585057	0.561185	0.063*
H26C	0.216388	0.575950	0.438222	0.063*
C27	0.44892 (18)	0.55442 (6)	0.51818 (19)	0.0483 (5)
H27A	0.413118	0.532945	0.467719	0.072*
H27B	0.444629	0.547685	0.587207	0.072*
H27C	0.523174	0.555953	0.523061	0.072*
C28	0.45209 (15)	0.63728 (7)	0.58702 (14)	0.0386 (4)
H28A	0.524819	0.642292	0.589825	0.058*
H28B	0.452689	0.623560	0.651760	0.058*
H28C	0.414578	0.663656	0.579768	0.058*
Fe2	1.06717 (2)	0.59728 (2)	0.73660 (2)	0.01677 (5)
S2	0.86582 (3)	0.79761 (2)	0.67762 (3)	0.01875 (7)
P3	1.20661 (3)	0.63524 (2)	0.82008 (3)	0.02169 (8)
P4	1.05319 (3)	0.56362 (2)	0.87131 (3)	0.02180 (8)
O2	1.21287 (10)	0.53829 (4)	0.69799 (10)	0.0350 (3)
N4	0.98932 (9)	0.67679 (4)	0.78335 (9)	0.0182 (2)
N5	0.96964 (9)	0.64174 (4)	0.72141 (9)	0.0171 (2)
N6	0.94560 (10)	0.57373 (4)	0.62879 (9)	0.0210 (2)
C29	0.88599 (11)	0.84938 (4)	0.71594 (12)	0.0184 (3)
C30	0.86403 (11)	0.88323 (5)	0.64814 (13)	0.0233 (3)
H30	0.833657	0.879685	0.574355	0.028*
C31	0.88807 (13)	0.92220 (5)	0.69217 (14)	0.0276 (3)
H31	0.874472	0.945738	0.647704	0.033*
C32	0.93179 (13)	0.92747 (5)	0.80038 (15)	0.0287 (3)
H32	0.946909	0.954560	0.828425	0.034*
C33	0.95368 (12)	0.89386 (5)	0.86800 (13)	0.0239 (3)
H33	0.983475	0.897741	0.941717	0.029*
C34	0.93101 (11)	0.85410 (4)	0.82548 (12)	0.0189 (3)
C35	0.92194 (10)	0.78126 (4)	0.80860 (11)	0.0171 (3)
C36	0.95100 (11)	0.81457 (4)	0.87915 (11)	0.0178 (3)

C37	0.99331 (12)	0.80680 (5)	0.98707 (12)	0.0226 (3)
H37	1.011412	0.829011	1.035756	0.027*
C38	1.00841 (13)	0.76631 (5)	1.02188 (12)	0.0253 (3)
H38	1.035745	0.760779	1.095041	0.030*
C39	0.98387 (12)	0.73344 (5)	0.95052 (12)	0.0235 (3)
H39	0.996967	0.705941	0.976125	0.028*
C40	0.94065 (11)	0.74017 (4)	0.84278 (11)	0.0186 (3)
C41	0.91399 (11)	0.70474 (4)	0.76852 (11)	0.0186 (3)
C42	0.81208 (11)	0.70174 (5)	0.69147 (12)	0.0210 (3)
H42	0.762254	0.723579	0.679550	0.025*
C43	0.78924 (12)	0.66576 (5)	0.63519 (11)	0.0210 (3)
H43	0.721168	0.661503	0.584742	0.025*
C44	0.86699 (11)	0.63537 (4)	0.65263 (11)	0.0189 (3)
C45	0.85334 (12)	0.59607 (4)	0.60339 (11)	0.0210 (3)
C46	0.75592 (14)	0.57940 (5)	0.53921 (13)	0.0284 (3)
H46	0.693186	0.595298	0.523872	0.034*
C47	0.75179 (15)	0.54039 (5)	0.49910 (13)	0.0329 (4)
H47	0.686507	0.528614	0.457233	0.039*
C48	0.84680 (15)	0.51813 (5)	0.52147 (13)	0.0316 (4)
H48	0.846718	0.491330	0.492899	0.038*
C49	0.93895 (14)	0.53533 (5)	0.58444 (12)	0.0266 (3)
H49	1.002109	0.519805	0.598322	0.032*
C50	1.15461 (13)	0.56265 (5)	0.71191 (12)	0.0239 (3)
C51	1.22180 (15)	0.68063 (6)	0.74707 (16)	0.0360 (4)
H51A	1.225619	0.672082	0.678987	0.054*
H51B	1.286782	0.695225	0.786874	0.054*
H51C	1.161171	0.699030	0.736038	0.054*
C52	1.22545 (14)	0.65821 (6)	0.94861 (13)	0.0319 (4)
H52A	1.162822	0.674345	0.945412	0.048*
H52B	1.287421	0.676315	0.968223	0.048*
H52C	1.236191	0.636259	1.001044	0.048*
C53	1.33634 (13)	0.61128 (6)	0.84742 (16)	0.0352 (4)
H53A	1.342898	0.587641	0.894428	0.053*
H53B	1.391603	0.631508	0.880919	0.053*
H53C	1.343967	0.601847	0.781548	0.053*
C54	0.96084 (15)	0.52024 (5)	0.83666 (14)	0.0322 (4)
H54A	0.889850	0.530472	0.797736	0.048*
H54B	0.960213	0.506353	0.900773	0.048*
H54C	0.982970	0.500661	0.792901	0.048*
C55	1.17149 (14)	0.53884 (6)	0.96047 (14)	0.0340 (4)
H55A	1.202824	0.521050	0.920264	0.051*
H55B	1.152500	0.522139	1.011815	0.051*
H55C	1.222594	0.560041	0.997153	0.051*
C56	1.00203 (15)	0.59247 (6)	0.95985 (14)	0.0337 (4)
H56A	1.046068	0.616895	0.985942	0.051*
H56B	1.003260	0.574851	1.019124	0.051*
H56C	0.929324	0.601124	0.921955	0.051*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.01493 (10)	0.02206 (11)	0.02349 (11)	−0.00260 (7)	0.00833 (8)	−0.00272 (8)
S1	0.0319 (2)	0.02150 (18)	0.02929 (19)	−0.00082 (15)	0.01718 (17)	−0.00173 (15)
P1	0.01522 (17)	0.0289 (2)	0.02408 (19)	0.00079 (14)	0.00856 (15)	−0.00361 (15)
P2	0.02358 (19)	0.0303 (2)	0.0277 (2)	−0.00653 (16)	0.01035 (17)	0.00340 (17)
O1	0.0299 (7)	0.0471 (8)	0.0618 (10)	−0.0133 (6)	0.0081 (7)	−0.0225 (7)
N1	0.0170 (6)	0.0216 (6)	0.0219 (6)	−0.0009 (4)	0.0077 (5)	−0.0015 (5)
N2	0.0164 (5)	0.0190 (6)	0.0207 (6)	0.0004 (4)	0.0080 (5)	0.0000 (5)
N3	0.0206 (6)	0.0210 (6)	0.0248 (6)	−0.0009 (5)	0.0092 (5)	−0.0003 (5)
C1	0.0201 (7)	0.0223 (7)	0.0281 (8)	−0.0001 (6)	0.0038 (6)	−0.0017 (6)
C2	0.0310 (9)	0.0289 (8)	0.0408 (10)	−0.0016 (7)	0.0145 (8)	0.0022 (7)
C3	0.0304 (9)	0.0254 (8)	0.0521 (11)	−0.0039 (7)	0.0103 (8)	0.0042 (8)
C4	0.0243 (8)	0.0220 (8)	0.0467 (10)	−0.0007 (6)	−0.0001 (8)	−0.0057 (7)
C5	0.0225 (7)	0.0262 (8)	0.0339 (9)	0.0006 (6)	0.0007 (7)	−0.0079 (7)
C6	0.0158 (6)	0.0250 (7)	0.0251 (7)	−0.0005 (5)	−0.0005 (6)	−0.0051 (6)
C7	0.0147 (6)	0.0261 (7)	0.0197 (7)	−0.0007 (5)	0.0042 (5)	−0.0037 (6)
C8	0.0165 (6)	0.0249 (7)	0.0216 (7)	−0.0005 (5)	0.0012 (6)	−0.0060 (6)
C9	0.0275 (8)	0.0317 (8)	0.0261 (8)	−0.0016 (6)	0.0087 (7)	−0.0127 (7)
C10	0.0305 (8)	0.0396 (9)	0.0246 (8)	−0.0060 (7)	0.0133 (7)	−0.0093 (7)
C11	0.0235 (7)	0.0314 (8)	0.0222 (7)	−0.0048 (6)	0.0083 (6)	−0.0047 (6)
C12	0.0154 (6)	0.0251 (7)	0.0197 (6)	−0.0007 (5)	0.0045 (5)	−0.0030 (6)
C13	0.0173 (6)	0.0211 (7)	0.0189 (6)	0.0008 (5)	0.0058 (5)	0.0010 (5)
C14	0.0163 (6)	0.0223 (7)	0.0281 (7)	−0.0023 (5)	0.0082 (6)	0.0013 (6)
C15	0.0154 (6)	0.0235 (7)	0.0280 (7)	0.0023 (5)	0.0101 (6)	0.0027 (6)
C16	0.0149 (6)	0.0209 (7)	0.0191 (6)	0.0021 (5)	0.0068 (5)	0.0035 (5)
C17	0.0185 (6)	0.0200 (7)	0.0202 (7)	0.0017 (5)	0.0074 (6)	0.0031 (5)
C18	0.0216 (7)	0.0228 (7)	0.0293 (8)	0.0040 (6)	0.0112 (6)	0.0034 (6)
C19	0.0290 (8)	0.0255 (8)	0.0310 (8)	0.0070 (6)	0.0131 (7)	0.0001 (6)
C20	0.0332 (9)	0.0218 (8)	0.0358 (9)	−0.0002 (6)	0.0121 (7)	−0.0050 (7)
C21	0.0286 (8)	0.0224 (8)	0.0371 (9)	−0.0044 (6)	0.0126 (7)	−0.0048 (7)
C22	0.0233 (8)	0.0328 (9)	0.0357 (9)	−0.0017 (6)	0.0107 (7)	−0.0079 (7)
C23	0.0161 (7)	0.0457 (11)	0.0442 (10)	0.0005 (7)	0.0069 (7)	−0.0062 (8)
C24	0.0289 (8)	0.0390 (10)	0.0320 (9)	0.0040 (7)	0.0164 (7)	−0.0068 (7)
C25	0.0270 (8)	0.0296 (8)	0.0266 (8)	0.0050 (6)	0.0092 (7)	0.0002 (6)
C26	0.0353 (10)	0.0569 (13)	0.0407 (10)	−0.0166 (9)	0.0206 (9)	0.0025 (9)
C27	0.0514 (12)	0.0376 (11)	0.0561 (13)	0.0040 (9)	0.0186 (11)	0.0183 (10)
C28	0.0373 (10)	0.0510 (11)	0.0256 (8)	−0.0112 (8)	0.0081 (8)	0.0012 (8)
Fe2	0.02222 (10)	0.01360 (10)	0.01504 (9)	0.00217 (7)	0.00699 (8)	−0.00007 (7)
S2	0.01849 (16)	0.01793 (16)	0.01829 (15)	0.00061 (12)	0.00416 (13)	−0.00110 (13)
P3	0.02033 (18)	0.02093 (18)	0.02220 (18)	0.00205 (14)	0.00503 (15)	−0.00170 (14)
P4	0.02679 (19)	0.02252 (19)	0.01832 (17)	0.00484 (15)	0.01053 (15)	0.00397 (14)
O2	0.0410 (7)	0.0282 (6)	0.0391 (7)	0.0111 (5)	0.0177 (6)	−0.0055 (5)
N4	0.0203 (6)	0.0151 (5)	0.0181 (5)	0.0013 (4)	0.0049 (5)	−0.0019 (4)
N5	0.0208 (6)	0.0141 (5)	0.0152 (5)	−0.0003 (4)	0.0045 (5)	−0.0007 (4)
N6	0.0314 (7)	0.0159 (6)	0.0159 (5)	−0.0019 (5)	0.0084 (5)	−0.0018 (4)
C29	0.0134 (6)	0.0176 (6)	0.0248 (7)	0.0004 (5)	0.0074 (6)	−0.0010 (5)

C30	0.0179 (7)	0.0235 (7)	0.0297 (8)	−0.0002 (5)	0.0094 (6)	0.0032 (6)
C31	0.0258 (8)	0.0204 (7)	0.0396 (9)	−0.0014 (6)	0.0149 (7)	0.0050 (7)
C32	0.0285 (8)	0.0179 (7)	0.0431 (10)	−0.0048 (6)	0.0165 (7)	−0.0052 (7)
C33	0.0218 (7)	0.0217 (7)	0.0305 (8)	−0.0037 (6)	0.0116 (6)	−0.0070 (6)
C34	0.0137 (6)	0.0193 (7)	0.0259 (7)	0.0000 (5)	0.0094 (6)	−0.0029 (6)
C35	0.0139 (6)	0.0194 (7)	0.0176 (6)	0.0017 (5)	0.0049 (5)	−0.0009 (5)
C36	0.0134 (6)	0.0194 (7)	0.0215 (7)	0.0014 (5)	0.0071 (5)	−0.0038 (5)
C37	0.0217 (7)	0.0249 (7)	0.0212 (7)	0.0011 (6)	0.0072 (6)	−0.0064 (6)
C38	0.0290 (8)	0.0283 (8)	0.0170 (7)	0.0040 (6)	0.0057 (6)	−0.0008 (6)
C39	0.0257 (7)	0.0219 (7)	0.0212 (7)	0.0047 (6)	0.0058 (6)	0.0012 (6)
C40	0.0163 (6)	0.0187 (7)	0.0203 (6)	0.0026 (5)	0.0056 (5)	−0.0024 (5)
C41	0.0205 (7)	0.0164 (6)	0.0189 (6)	0.0008 (5)	0.0067 (6)	0.0009 (5)
C42	0.0186 (7)	0.0193 (7)	0.0236 (7)	0.0026 (5)	0.0053 (6)	0.0023 (6)
C43	0.0192 (7)	0.0215 (7)	0.0190 (6)	−0.0019 (5)	0.0021 (6)	0.0029 (5)
C44	0.0223 (7)	0.0172 (7)	0.0159 (6)	−0.0018 (5)	0.0046 (6)	0.0015 (5)
C45	0.0271 (7)	0.0191 (7)	0.0155 (6)	−0.0032 (5)	0.0052 (6)	0.0010 (5)
C46	0.0314 (8)	0.0254 (8)	0.0223 (7)	−0.0061 (6)	0.0011 (7)	0.0001 (6)
C47	0.0406 (10)	0.0274 (8)	0.0247 (8)	−0.0136 (7)	0.0032 (7)	−0.0032 (6)
C48	0.0516 (11)	0.0201 (7)	0.0234 (7)	−0.0100 (7)	0.0130 (8)	−0.0061 (6)
C49	0.0425 (9)	0.0177 (7)	0.0221 (7)	−0.0029 (6)	0.0143 (7)	−0.0026 (6)
C50	0.0320 (8)	0.0200 (7)	0.0209 (7)	0.0008 (6)	0.0107 (6)	0.0002 (6)
C51	0.0334 (9)	0.0299 (9)	0.0422 (10)	−0.0084 (7)	0.0093 (8)	0.0046 (8)
C52	0.0268 (8)	0.0351 (9)	0.0280 (8)	0.0031 (7)	0.0015 (7)	−0.0101 (7)
C53	0.0226 (8)	0.0390 (10)	0.0423 (10)	0.0048 (7)	0.0085 (7)	−0.0075 (8)
C54	0.0405 (10)	0.0286 (8)	0.0325 (9)	−0.0024 (7)	0.0188 (8)	0.0058 (7)
C55	0.0349 (9)	0.0385 (10)	0.0288 (8)	0.0096 (7)	0.0110 (7)	0.0135 (7)
C56	0.0387 (9)	0.0427 (10)	0.0244 (8)	0.0059 (8)	0.0168 (7)	−0.0033 (7)

Geometric parameters (Å, °)

Fe1—P1	2.2144 (4)	Fe2—P3	2.2087 (4)
Fe1—P2	2.1847 (5)	Fe2—P4	2.1862 (4)
Fe1—N2	1.9054 (12)	Fe2—N5	1.9117 (12)
Fe1—N3	1.9464 (13)	Fe2—N6	1.9434 (13)
Fe1—C22	1.7426 (17)	Fe2—C50	1.7371 (16)
S1—C1	1.7538 (16)	S2—C29	1.7486 (15)
S1—C7	1.7547 (16)	S2—C35	1.7582 (14)
P1—C23	1.8261 (17)	P3—C51	1.8207 (18)
P1—C24	1.8382 (17)	P3—C52	1.8294 (17)
P1—C25	1.8254 (17)	P3—C53	1.8304 (17)
P2—C26	1.8258 (19)	P4—C54	1.8284 (18)
P2—C27	1.830 (2)	P4—C55	1.8271 (17)
P2—C28	1.8312 (19)	P4—C56	1.8272 (17)
O1—C22	1.169 (2)	O2—C50	1.1713 (19)
N1—N2	1.3736 (17)	N4—N5	1.3826 (16)
N1—C13	1.3224 (19)	N4—C41	1.3228 (18)
N2—C16	1.3954 (18)	N5—C44	1.3964 (18)
N3—C17	1.3830 (19)	N6—C45	1.377 (2)

N3—C21	1.375 (2)	N6—C49	1.3704 (19)
C1—C2	1.397 (2)	C29—C30	1.396 (2)
C1—C6	1.401 (2)	C29—C34	1.408 (2)
C2—H2	0.9500	C30—H30	0.9500
C2—C3	1.386 (3)	C30—C31	1.386 (2)
C3—H3	0.9500	C31—H31	0.9500
C3—C4	1.395 (3)	C31—C32	1.393 (3)
C4—H4	0.9500	C32—H32	0.9500
C4—C5	1.382 (3)	C32—C33	1.388 (2)
C5—H5	0.9500	C33—H33	0.9500
C5—C6	1.401 (2)	C33—C34	1.401 (2)
C6—C8	1.449 (2)	C34—C36	1.451 (2)
C7—C8	1.410 (2)	C35—C36	1.406 (2)
C7—C12	1.404 (2)	C35—C40	1.403 (2)
C8—C9	1.397 (2)	C36—C37	1.400 (2)
C9—H9	0.9500	C37—H37	0.9500
C9—C10	1.375 (3)	C37—C38	1.385 (2)
C10—H10	0.9500	C38—H38	0.9500
C10—C11	1.397 (2)	C38—C39	1.400 (2)
C11—H11	0.9500	C39—H39	0.9500
C11—C12	1.394 (2)	C39—C40	1.393 (2)
C12—C13	1.489 (2)	C40—C41	1.487 (2)
C13—C14	1.420 (2)	C41—C42	1.419 (2)
C14—H14	0.9500	C42—H42	0.9500
C14—C15	1.368 (2)	C42—C43	1.369 (2)
C15—H15	0.9500	C43—H43	0.9500
C15—C16	1.401 (2)	C43—C44	1.397 (2)
C16—C17	1.411 (2)	C44—C45	1.419 (2)
C17—C18	1.412 (2)	C45—C46	1.413 (2)
C18—H18	0.9500	C46—H46	0.9500
C18—C19	1.365 (2)	C46—C47	1.369 (2)
C19—H19	0.9500	C47—H47	0.9500
C19—C20	1.408 (2)	C47—C48	1.409 (3)
C20—H20	0.9500	C48—H48	0.9500
C20—C21	1.368 (2)	C48—C49	1.364 (2)
C21—H21	0.9500	C49—H49	0.9500
C23—H23A	0.9800	C51—H51A	0.9800
C23—H23B	0.9800	C51—H51B	0.9800
C23—H23C	0.9800	C51—H51C	0.9800
C24—H24A	0.9800	C52—H52A	0.9800
C24—H24B	0.9800	C52—H52B	0.9800
C24—H24C	0.9800	C52—H52C	0.9800
C25—H25A	0.9800	C53—H53A	0.9800
C25—H25B	0.9800	C53—H53B	0.9800
C25—H25C	0.9800	C53—H53C	0.9800
C26—H26A	0.9800	C54—H54A	0.9800
C26—H26B	0.9800	C54—H54B	0.9800
C26—H26C	0.9800	C54—H54C	0.9800

C27—H27A	0.9800	C55—H55A	0.9800
C27—H27B	0.9800	C55—H55B	0.9800
C27—H27C	0.9800	C55—H55C	0.9800
C28—H28A	0.9800	C56—H56A	0.9800
C28—H28B	0.9800	C56—H56B	0.9800
C28—H28C	0.9800	C56—H56C	0.9800
H9...C17 ⁱ	2.676	H23C...C34 ⁱⁱⁱ	2.824
H15...C34 ⁱⁱ	2.704	H25C...C52 ^v	2.834
H2...C43 ⁱⁱ	2.730	H49 ^{vi} ...H32 ⁱⁱⁱ	2.336
C8...H53B ⁱⁱⁱ	2.755	C6...H30	2.841
H15...C36 ⁱⁱ	2.770	H23B...S2 ⁱⁱⁱ	2.943
S1...C42 ⁱⁱ	3.389	H5...C19 ⁱ	2.843
O2...H48 ^{iv}	2.616	H19...O2 ^{iv}	2.664
H18...C32 ⁱⁱ	2.798		
P2—Fe1—P1	99.457 (18)	P4—Fe2—P3	98.499 (17)
N2—Fe1—P1	91.04 (4)	N5—Fe2—P3	94.01 (4)
N2—Fe1—P2	102.65 (4)	N5—Fe2—P4	102.48 (4)
N2—Fe1—N3	80.70 (5)	N5—Fe2—N6	80.86 (5)
N3—Fe1—P1	153.19 (4)	N6—Fe2—P3	163.19 (4)
N3—Fe1—P2	107.22 (4)	N6—Fe2—P4	98.24 (4)
C22—Fe1—P1	88.71 (6)	C50—Fe2—P3	86.79 (5)
C22—Fe1—P2	93.24 (6)	C50—Fe2—P4	95.33 (5)
C22—Fe1—N2	163.93 (7)	C50—Fe2—N5	161.83 (6)
C22—Fe1—N3	92.38 (7)	C50—Fe2—N6	93.19 (7)
C1—S1—C7	91.40 (8)	C29—S2—C35	91.07 (7)
C23—P1—Fe1	115.71 (7)	C51—P3—Fe2	113.76 (6)
C23—P1—C24	100.05 (8)	C51—P3—C52	100.55 (9)
C24—P1—Fe1	123.45 (6)	C51—P3—C53	100.26 (9)
C25—P1—Fe1	113.27 (5)	C52—P3—Fe2	122.29 (6)
C25—P1—C23	100.13 (9)	C52—P3—C53	99.38 (8)
C25—P1—C24	100.75 (8)	C53—P3—Fe2	117.08 (6)
C26—P2—Fe1	117.72 (7)	C54—P4—Fe2	114.27 (6)
C26—P2—C27	100.80 (10)	C55—P4—Fe2	117.97 (6)
C26—P2—C28	101.83 (10)	C55—P4—C54	101.40 (9)
C27—P2—Fe1	114.64 (8)	C55—P4—C56	103.19 (9)
C27—P2—C28	101.53 (11)	C56—P4—Fe2	116.71 (6)
C28—P2—Fe1	117.66 (6)	C56—P4—C54	100.79 (9)
C13—N1—N2	119.81 (12)	C41—N4—N5	119.30 (12)
N1—N2—Fe1	123.88 (9)	N4—N5—Fe2	124.66 (9)
N1—N2—C16	118.74 (12)	N4—N5—C44	118.02 (11)
C16—N2—Fe1	117.26 (10)	C44—N5—Fe2	116.70 (9)
C17—N3—Fe1	116.15 (10)	C45—N6—Fe2	116.19 (10)
C21—N3—Fe1	127.66 (11)	C49—N6—Fe2	126.80 (11)
C21—N3—C17	116.18 (13)	C49—N6—C45	116.56 (13)
C2—C1—S1	126.37 (14)	C30—C29—S2	125.48 (12)
C2—C1—C6	121.30 (15)	C30—C29—C34	121.85 (14)

C6—C1—S1	112.33 (12)	C34—C29—S2	112.64 (11)
C1—C2—H2	120.8	C29—C30—H30	121.1
C3—C2—C1	118.48 (18)	C31—C30—C29	117.71 (15)
C3—C2—H2	120.8	C31—C30—H30	121.1
C2—C3—H3	119.6	C30—C31—H31	119.4
C2—C3—C4	120.83 (17)	C30—C31—C32	121.23 (15)
C4—C3—H3	119.6	C32—C31—H31	119.4
C3—C4—H4	119.7	C31—C32—H32	119.4
C5—C4—C3	120.63 (16)	C33—C32—C31	121.17 (15)
C5—C4—H4	119.7	C33—C32—H32	119.4
C4—C5—H5	120.2	C32—C33—H33	120.6
C4—C5—C6	119.60 (17)	C32—C33—C34	118.76 (15)
C6—C5—H5	120.2	C34—C33—H33	120.6
C1—C6—C5	119.16 (16)	C29—C34—C36	111.88 (12)
C1—C6—C8	112.15 (14)	C33—C34—C29	119.27 (14)
C5—C6—C8	128.69 (16)	C33—C34—C36	128.81 (14)
C8—C7—S1	111.88 (12)	C36—C35—S2	112.35 (11)
C12—C7—S1	126.64 (11)	C40—C35—S2	125.90 (11)
C12—C7—C8	121.45 (14)	C40—C35—C36	121.71 (13)
C7—C8—C6	112.24 (14)	C35—C36—C34	111.99 (13)
C9—C8—C6	128.45 (14)	C37—C36—C34	128.48 (13)
C9—C8—C7	119.29 (15)	C37—C36—C35	119.53 (13)
C8—C9—H9	120.1	C36—C37—H37	120.4
C10—C9—C8	119.73 (15)	C38—C37—C36	119.11 (14)
C10—C9—H9	120.1	C38—C37—H37	120.4
C9—C10—H10	119.7	C37—C38—H38	119.6
C9—C10—C11	120.65 (15)	C37—C38—C39	120.78 (14)
C11—C10—H10	119.7	C39—C38—H38	119.6
C10—C11—H11	119.3	C38—C39—H39	119.3
C12—C11—C10	121.47 (16)	C40—C39—C38	121.43 (14)
C12—C11—H11	119.3	C40—C39—H39	119.3
C7—C12—C13	123.21 (13)	C35—C40—C41	122.20 (13)
C11—C12—C7	117.37 (14)	C39—C40—C35	117.30 (13)
C11—C12—C13	119.40 (14)	C39—C40—C41	120.49 (13)
N1—C13—C12	113.63 (12)	N4—C41—C40	115.29 (12)
N1—C13—C14	123.87 (14)	N4—C41—C42	124.46 (13)
C14—C13—C12	122.46 (13)	C42—C41—C40	120.19 (13)
C13—C14—H14	121.7	C41—C42—H42	121.7
C15—C14—C13	116.64 (13)	C43—C42—C41	116.58 (13)
C15—C14—H14	121.7	C43—C42—H42	121.7
C14—C15—H15	120.0	C42—C43—H43	120.3
C14—C15—C16	119.95 (13)	C42—C43—C44	119.37 (13)
C16—C15—H15	120.0	C44—C43—H43	120.3
N2—C16—C15	120.66 (13)	N5—C44—C43	121.65 (13)
N2—C16—C17	112.76 (12)	N5—C44—C45	112.81 (13)
C15—C16—C17	126.55 (13)	C43—C44—C45	125.53 (14)
N3—C17—C16	113.11 (12)	N6—C45—C44	113.00 (13)
N3—C17—C18	121.58 (14)	N6—C45—C46	121.63 (14)

C16—C17—C18	125.30 (14)	C46—C45—C44	125.28 (15)
C17—C18—H18	119.8	C45—C46—H46	119.9
C19—C18—C17	120.39 (15)	C47—C46—C45	120.11 (16)
C19—C18—H18	119.8	C47—C46—H46	119.9
C18—C19—H19	120.8	C46—C47—H47	120.8
C18—C19—C20	118.38 (15)	C46—C47—C48	118.31 (16)
C20—C19—H19	120.8	C48—C47—H47	120.8
C19—C20—H20	120.2	C47—C48—H48	120.2
C21—C20—C19	119.53 (15)	C49—C48—C47	119.56 (15)
C21—C20—H20	120.2	C49—C48—H48	120.2
N3—C21—H21	118.1	N6—C49—H49	118.1
C20—C21—N3	123.81 (15)	C48—C49—N6	123.73 (16)
C20—C21—H21	118.1	C48—C49—H49	118.1
O1—C22—Fe1	177.53 (18)	O2—C50—Fe2	177.43 (14)
P1—C23—H23A	109.5	P3—C51—H51A	109.5
P1—C23—H23B	109.5	P3—C51—H51B	109.5
P1—C23—H23C	109.5	P3—C51—H51C	109.5
H23A—C23—H23B	109.5	H51A—C51—H51B	109.5
H23A—C23—H23C	109.5	H51A—C51—H51C	109.5
H23B—C23—H23C	109.5	H51B—C51—H51C	109.5
P1—C24—H24A	109.5	P3—C52—H52A	109.5
P1—C24—H24B	109.5	P3—C52—H52B	109.5
P1—C24—H24C	109.5	P3—C52—H52C	109.5
H24A—C24—H24B	109.5	H52A—C52—H52B	109.5
H24A—C24—H24C	109.5	H52A—C52—H52C	109.5
H24B—C24—H24C	109.5	H52B—C52—H52C	109.5
P1—C25—H25A	109.5	P3—C53—H53A	109.5
P1—C25—H25B	109.5	P3—C53—H53B	109.5
P1—C25—H25C	109.5	P3—C53—H53C	109.5
H25A—C25—H25B	109.5	H53A—C53—H53B	109.5
H25A—C25—H25C	109.5	H53A—C53—H53C	109.5
H25B—C25—H25C	109.5	H53B—C53—H53C	109.5
P2—C26—H26A	109.5	P4—C54—H54A	109.5
P2—C26—H26B	109.5	P4—C54—H54B	109.5
P2—C26—H26C	109.5	P4—C54—H54C	109.5
H26A—C26—H26B	109.5	H54A—C54—H54B	109.5
H26A—C26—H26C	109.5	H54A—C54—H54C	109.5
H26B—C26—H26C	109.5	H54B—C54—H54C	109.5
P2—C27—H27A	109.5	P4—C55—H55A	109.5
P2—C27—H27B	109.5	P4—C55—H55B	109.5
P2—C27—H27C	109.5	P4—C55—H55C	109.5
H27A—C27—H27B	109.5	H55A—C55—H55B	109.5
H27A—C27—H27C	109.5	H55A—C55—H55C	109.5
H27B—C27—H27C	109.5	H55B—C55—H55C	109.5
P2—C28—H28A	109.5	P4—C56—H56A	109.5
P2—C28—H28B	109.5	P4—C56—H56B	109.5
P2—C28—H28C	109.5	P4—C56—H56C	109.5
H28A—C28—H28B	109.5	H56A—C56—H56B	109.5

H28A—C28—H28C	109.5	H56A—C56—H56C	109.5
H28B—C28—H28C	109.5	H56B—C56—H56C	109.5
Fe1—N2—C16—C15	177.72 (11)	Fe2—N5—C44—C43	−179.81 (11)
Fe1—N2—C16—C17	−0.56 (16)	Fe2—N5—C44—C45	−1.00 (16)
Fe1—N3—C17—C16	1.61 (16)	Fe2—N6—C45—C44	7.11 (16)
Fe1—N3—C17—C18	−177.05 (11)	Fe2—N6—C45—C46	−169.65 (12)
Fe1—N3—C21—C20	178.79 (14)	Fe2—N6—C49—C48	169.22 (13)
S1—C1—C2—C3	179.57 (14)	S2—C29—C30—C31	−178.05 (12)
S1—C1—C6—C5	−179.88 (12)	S2—C29—C34—C33	178.83 (11)
S1—C1—C6—C8	0.40 (16)	S2—C29—C34—C36	0.92 (15)
S1—C7—C8—C6	0.83 (16)	S2—C35—C36—C34	−2.24 (15)
S1—C7—C8—C9	179.46 (12)	S2—C35—C36—C37	177.62 (11)
S1—C7—C12—C11	−179.76 (12)	S2—C35—C40—C39	−178.63 (11)
S1—C7—C12—C13	−1.4 (2)	S2—C35—C40—C41	0.1 (2)
N1—N2—C16—C15	−6.2 (2)	N4—N5—C44—C43	8.8 (2)
N1—N2—C16—C17	175.51 (12)	N4—N5—C44—C45	−172.39 (12)
N1—C13—C14—C15	−3.2 (2)	N4—C41—C42—C43	5.3 (2)
N2—N1—C13—C12	−178.43 (12)	N5—N4—C41—C40	176.74 (12)
N2—N1—C13—C14	−0.8 (2)	N5—N4—C41—C42	−0.6 (2)
N2—C16—C17—N3	−0.68 (18)	N5—C44—C45—N6	−3.89 (18)
N2—C16—C17—C18	177.92 (14)	N5—C44—C45—C46	172.73 (14)
N3—C17—C18—C19	−2.7 (2)	N6—C45—C46—C47	−1.1 (2)
C1—S1—C7—C8	−0.51 (12)	C29—S2—C35—C36	2.34 (11)
C1—S1—C7—C12	177.29 (14)	C29—S2—C35—C40	−175.61 (13)
C1—C2—C3—C4	0.8 (3)	C29—C30—C31—C32	−0.5 (2)
C1—C6—C8—C7	−0.79 (18)	C29—C34—C36—C35	0.85 (17)
C1—C6—C8—C9	−179.26 (15)	C29—C34—C36—C37	−178.99 (14)
C2—C1—C6—C5	0.3 (2)	C30—C29—C34—C33	0.6 (2)
C2—C1—C6—C8	−179.40 (15)	C30—C29—C34—C36	−177.34 (13)
C2—C3—C4—C5	−0.7 (3)	C30—C31—C32—C33	0.5 (2)
C3—C4—C5—C6	0.3 (2)	C31—C32—C33—C34	0.0 (2)
C4—C5—C6—C1	−0.1 (2)	C32—C33—C34—C29	−0.6 (2)
C4—C5—C6—C8	179.53 (15)	C32—C33—C34—C36	176.94 (14)
C5—C6—C8—C7	179.52 (15)	C33—C34—C36—C35	−176.81 (14)
C5—C6—C8—C9	1.0 (3)	C33—C34—C36—C37	3.3 (2)
C6—C1—C2—C3	−0.7 (2)	C34—C29—C30—C31	0.0 (2)
C6—C8—C9—C10	178.74 (15)	C34—C36—C37—C38	−178.36 (14)
C7—S1—C1—C2	179.85 (15)	C35—S2—C29—C30	176.34 (13)
C7—S1—C1—C6	0.06 (12)	C35—S2—C29—C34	−1.85 (11)
C7—C8—C9—C10	0.4 (2)	C35—C36—C37—C38	1.8 (2)
C7—C12—C13—N1	−134.90 (15)	C35—C40—C41—N4	132.23 (14)
C7—C12—C13—C14	47.4 (2)	C35—C40—C41—C42	−50.3 (2)
C8—C7—C12—C11	−2.2 (2)	C36—C35—C40—C39	3.6 (2)
C8—C7—C12—C13	176.22 (13)	C36—C35—C40—C41	−177.64 (13)
C8—C9—C10—C11	−1.5 (3)	C36—C37—C38—C39	1.3 (2)
C9—C10—C11—C12	0.9 (3)	C37—C38—C39—C40	−2.0 (2)
C10—C11—C12—C7	1.0 (2)	C38—C39—C40—C35	−0.5 (2)

C10—C11—C12—C13	−177.47 (14)	C38—C39—C40—C41	−179.24 (14)
C11—C12—C13—N1	43.44 (19)	C39—C40—C41—N4	−49.0 (2)
C11—C12—C13—C14	−134.22 (16)	C39—C40—C41—C42	128.39 (16)
C12—C7—C8—C6	−177.10 (13)	C40—C35—C36—C34	175.81 (13)
C12—C7—C8—C9	1.5 (2)	C40—C35—C36—C37	−4.3 (2)
C12—C13—C14—C15	174.25 (14)	C40—C41—C42—C43	−171.86 (14)
C13—N1—N2—Fe1	−178.75 (10)	C41—N4—N5—Fe2	−177.03 (10)
C13—N1—N2—C16	5.46 (19)	C41—N4—N5—C44	−6.40 (19)
C13—C14—C15—C16	2.3 (2)	C41—C42—C43—C44	−2.8 (2)
C14—C15—C16—N2	2.2 (2)	C42—C43—C44—N5	−4.1 (2)
C14—C15—C16—C17	−179.76 (15)	C42—C43—C44—C45	177.30 (14)
C15—C16—C17—N3	−178.83 (14)	C43—C44—C45—N6	174.86 (14)
C15—C16—C17—C18	−0.2 (2)	C43—C44—C45—C46	−8.5 (2)
C16—C17—C18—C19	178.76 (15)	C44—C45—C46—C47	−177.45 (15)
C17—N3—C21—C20	−2.7 (2)	C45—N6—C49—C48	−2.7 (2)
C17—C18—C19—C20	−0.6 (2)	C45—C46—C47—C48	−1.5 (3)
C18—C19—C20—C21	2.1 (3)	C46—C47—C48—C49	2.0 (3)
C19—C20—C21—N3	−0.5 (3)	C47—C48—C49—N6	0.2 (3)
C21—N3—C17—C16	−177.08 (14)	C49—N6—C45—C44	179.90 (13)
C21—N3—C17—C18	4.3 (2)	C49—N6—C45—C46	3.1 (2)

Symmetry codes: (i) $x, -y+3/2, z+1/2$; (ii) $x, -y+3/2, z-1/2$; (iii) $x-1, -y+3/2, z-1/2$; (iv) $-x+2, -y+1, -z+1$; (v) $x-1, y, z-1$; (vi) $-x+1, -y+1, -z+1$.