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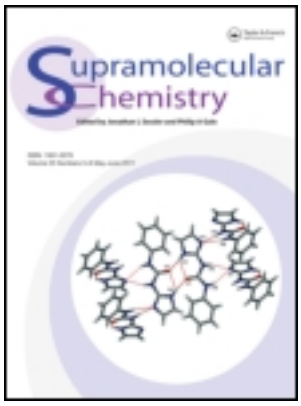

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Synthesis and characterisation of two high spin iron(II) complexes of 3,4-diphenyl-5-(2-pyridyl)-1,2,4-triazole

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Synthesis and characterisation of two high spin iron(II) complexes of 3,4-diphenyl-5-(2-pyridyl)-1,2,4-triazole

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The stepwise synthesis of the new ligand 4,5-diphenyl-3-pyridyl-1,2,4-triazole (phppt) from N-phenyl-pyridine-2-thiocarboxamide and benzohydrazide is reported. Two iron(II) complexes, $[Fe(phppt)_2(SCN)_2]\cdot 2MeOH$ and $[Fe(phppt)_2(SeCN)_2]\cdot Et_2O$, have been prepared and structurally characterised at 90 K, showing that both complexes are high spin (HS). The Mössbauer spectrum of $[Fe(phppt)_2(SeCN)_2]\cdot 1.5MeOH$ is consistent with the iron(II) ion being HS at 5.2 K.

Keywords: triazole; iron(II); high spin; Mössbauer spectrum; structure determination

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Introduction

Triazole-containing ligands have been shown previously to give a ligand field strength which is often appropriate for iron(II) spin crossover (*1–4*). This research group has developed an efficient pathway for the synthesis of both 4-R-3,5-dipyridyl-1,2,4-triazole (Rdpt) and 4-R-3-pyridyl-5-phenyl-1,2,4-triazole (Rppt) ligands (*5*). We (*6–10*) and others (*11–19*) have investigated the magnetic properties of a range of iron(II) complexes of such ligands (*3*). Spin crossover has been frequently observed, particularly in the case of the $[Fe(Rdpt)_2(NCE)_2]$ complexes (*3*, *6*, *7*, *9*, *11–19*).

Instead of the anticipated mononuclear complex, the 2:1 reaction of phdpt (Figure 1) with $[Fe(py)_4(SCN)_2]$ gave a trinuclear complex, $[Fe(phdpt)_4(SCN)_6]$, in which two of the Rdpt ligands are bis-bidentate (bridging) and two are bidentate (end capping) (*8*). This trinuclear complex was shown to be [HS-HS-HS], where HS = high spin, from 300 to 2 K. In order to restrict the number of possible binding modes and to facilitate the formation of a *mononuclear* $[Fe(Rdpt)_2(NCE)_2]$ complex, we turned our attention towards the synthesis of the diphenyl analogue of phdpt, phppt (Figure 1). The synthesis and characterisation of this new ligand and two iron(II) complexes of it are described herein.

Results and discussion

Synthesis of ligand

We have previously reported an effective synthetic route to synthesise 3,4,5 tri-substituted triazoles (*5*). It was extended to include the new triazole ligand phppt (Scheme 1). In the synthesis of the related ligand phdpt, it was found that the ethylation, step (ii), could be omitted if a longer reflux time was used. However, in the case of phppt, the latter method afforded only very low yields; ethylation of (**1**) to give (**2**) was found to be more successful. Analysis of the ^{1}H NMR spectrum of crude (**2**) indicated that the reaction did not proceed to completion. Attempts to purify (**2**) were unsuccessful, in large part because it is prone to decomposition. Purification proved unnecessary as the crude material was used successfully in the final step, (iii), to produce phppt which was readily purified by recrystallisation from methanol.

Synthesis of complexes

The 1:2 reactions, under argon at room temperature, of $[Fe(py)_4(ECN)_2]$ with E = S or Se with phppt in $MeOH/CHCl_3$ (4:1) gave red solutions. Pale orange block-shaped single crystals of $[Fe(phppt)_2(SCN)_2]\cdot 2MeOH$ (**3**·2MeOH) and a few orange single crystals of $[Fe(phppt)_2(SeCN)_2]\cdot Et_2O$ (**4**·Et_2O), suitable for X-ray crystallography (see the next section), were grown from these reaction solutions by vapour diffusion of diethyl ether under an argon atmosphere. Pure samples of both complexes were obtained by filtration under nitrogen and drying the solids under a flow of nitrogen. Both the crystal structure and elemental analysis data show that **3** is a methanol solvate, **3**·2MeOH. However, in the case of **4**, the single crystals are shown by the X-ray structure determination to be **4**·Et_2O, while microanalysis of the bulk sample, of orange microcrystals plus the few single crystals, fits best as a methanol solvate (between 1 and 2 MeOH; best fit is 1.5 MeOH, see experimental).

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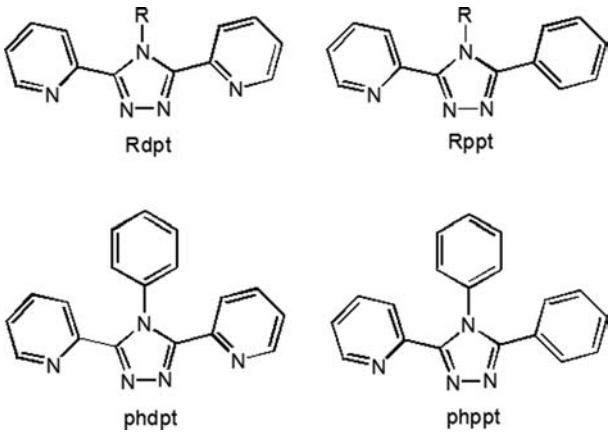


Figure 1. General structure of Rdpt and Rppt ligands, as well as the structure of 4-phenyl-3,5-di(2-pyridyl)-1,2,4-triazole (phdpt) and 4,5-diphenyl-3-pyridyl-1,2,4-triazole (phppt).

X-ray crystal structures of complexes

The crystal structure data for **3**·2MeOH and **4**·Et_2O were recorded at about 90 K; no change in colour was observed on cooling the crystals to this temperature. The complexes are isostructural (Figure 2). In both cases, half of the structure is present in the asymmetric unit with the other half being generated by a centre of inversion. The central iron(II) is bound to two bidentate phppt ligands, and to two ECN ligands orientated trans to each other. The bond lengths and angles observed are in the ranges expected for HS iron(II) (Table 1) (*20*).

In both structures, the triazole ring is not far from being coplanar with the pyridine ring at position 2 (Table 2; 25.5, 26.8°); however, a significant rotation is observed between the plane of the triazole ring and both of the phenyl groups, at positions 3 and 4 (Table 2; 43.2, 48.6° vs 65.5, 64.9°, respectively). As a result, the π overlap between the phenyl groups and central triazole will be poor and mesomeric effects will be limited. This is consistent with the results observed for complexes of other Rdpt ligands with aromatic substituents off the 4 position, and may help to explain why these ligands appear to give a relatively weak ligand field compared to other Rdpt ligands.

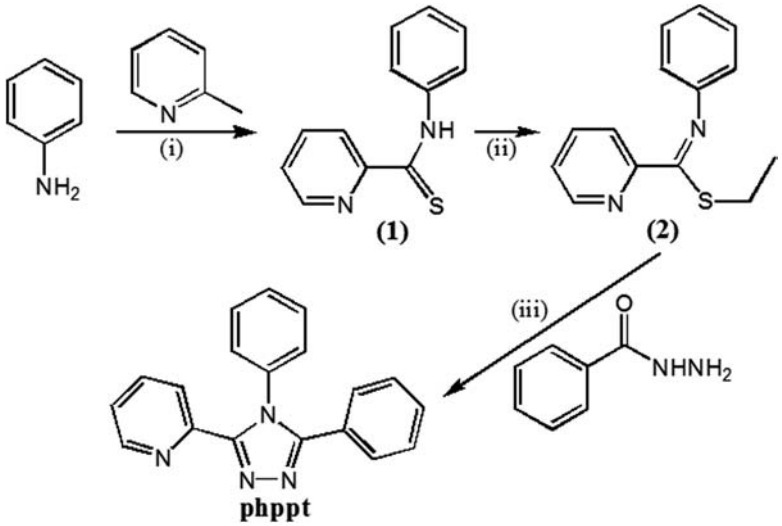
There are two half occupancy methanol molecules present in the asymmetric unit of **3**·2MeOH, which hydrogen bond to each other but do not make any significant interactions with the iron complex. There is a single ether molecule present in the asymmetric unit of **4**·Et_2O. It makes no significant interactions with the complex.

Mössbauer spectroscopy

The Mössbauer spectrum of **4**·1.5MeOH was recorded at 5.2 K (Figure 3) and consists of a single sharp quadrupole doublet. The isomer shift ($\delta = 1.15\,\mathrm{mm\,s^{-1}}$) and large quadrupole splitting ($\Delta E_q = 3.30\,\mathrm{mm\,s^{-1}}$) are highly characteristic of HS iron(II) (*21*). The parameters are very similar to those previously observed for related compounds (*6*, *8*).

Conclusion

A new triazole-based ligand, 4,5-diphenyl-3-pyridyl-1,2,4-triazole (phppt), and two iron(II) complexes of this ligand, $[Fe(phppt)_2(SCN)_2]$·2MeOH and $[Fe(phppt)_2(SeCN)_2]$·Et_2O, have been successfully synthesised and



Scheme 1. Synthetic pathway used to produce the new ligand phppt. (i) $Na_2S{\cdot}9H_2O$, S_8; (ii) ethyl bromide, NaOEt, EtOH reflux and (iii) BuOH reflux.

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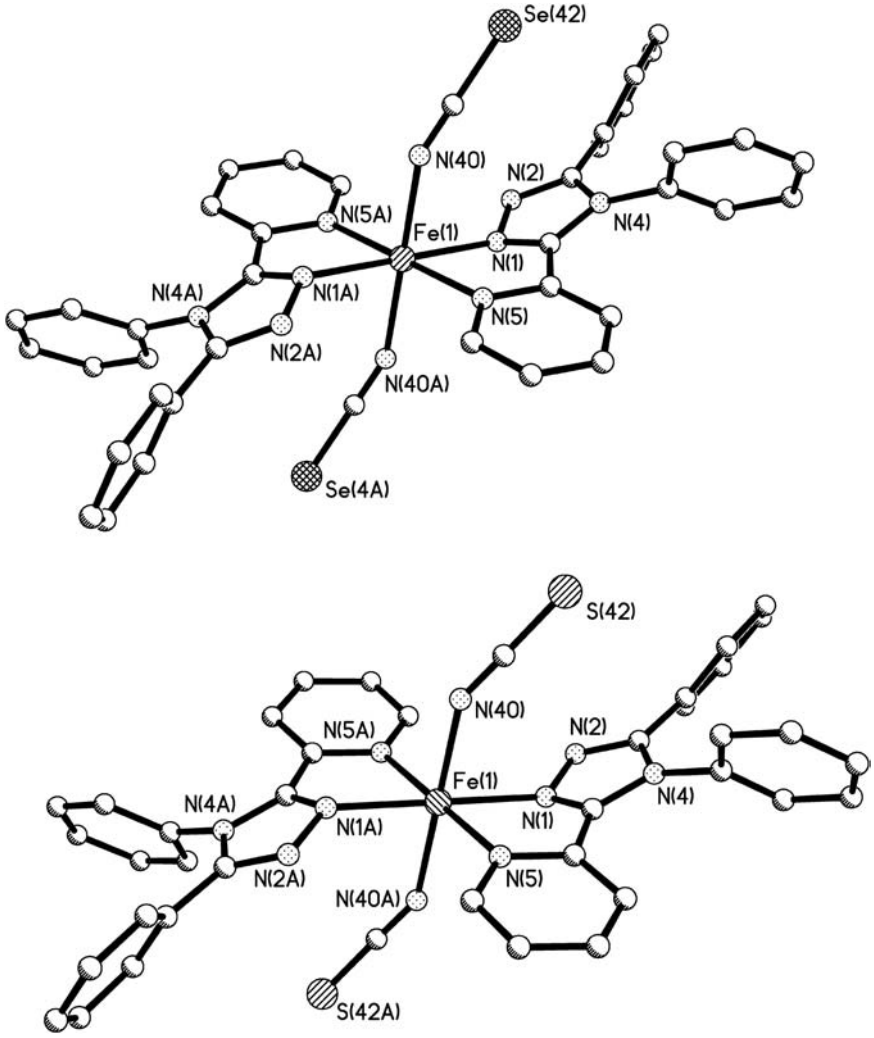

Figure 2. Perspective views of the complexes: (top) $[Fe(phppt)_2(SeCN)_2]\cdot Et_2O$ (**4**·Et_2O) and (bottom) $[Fe(phppt)_2(SCN)_2]\cdot 2MeOH$ (**3**·2MeOH). Hydrogen atoms and solvent molecules have been omitted for clarity.

characterised. The X-ray crystal structures of both complexes clearly indicate that the iron(II) ions are HS at 90 K. In addition, the low temperature (5.2 K), Mössbauer spectrum of $[Fe(phppt)_2(SeCN)_2]\cdot 1.5MeOH$ shows that this complex remains HS. As this complex involves the higher field anion NCSe, rather than NCS, current efforts are focused on the synthesis of new ligands which will impose a higher ligand field than phppt does, so that new generations of iron(II) spin crossover complexes can be accessed.

Table 1. Selected bond lengths [Å] and angles [°] for $[Fe(phppt)_2(SCN)_2]\cdot 2MeOH$ and $[Fe(phppt)_2(SeCN)_2]\cdot Et_2O$, at 89 and 91 K, respectively. Symmetry transformations used to generate equivalent atoms A $-x+1, -y, -z+1$.

	$[Fe(phppt)_2(SeCN)_2]\cdot Et_2O$	$[Fe(phppt)_2(SCN)_2]\cdot 2MeOH$
Fe(1)-N(40)	2.128(3)	2.126(2)
Fe(1)-N(1)	2.178(2)	2.189(2)
Fe(1)-N(5)	2.178(2)	2.186(2)
N(40)-Fe(1)-N(1)	83.60(10)	84.33(9)
N(40)-Fe(1)-N(1A)	96.40(10)	95.67(9)
N(40)-Fe(1)-N(5A)	90.93(10)	89.83(8)
N(1)-Fe(1)-N(5A)	103.59(9)	103.60(8)
N(40)-Fe(1)-N(5)	89.07(10)	90.17(8)
N(1)-Fe(1)-N(5)	76.41(9)	76.40(8)

Table 2. Angles [°] between mean plane of the triazole and the specified rings for $[Fe(phppt)_2(SCN)_2]\cdot 2MeOH$ and $[Fe(phppt)_2(SeCN)_2]\cdot Et_2O$.

	2-Pyridine	3-Phenyl	4-Phenyl
(**3**·2MeOH) Triazole	26.8(2)	43.2(1)	65.5(1)
(**4**·Et_2O) Triazole	25.5(2)	48.6(1)	64.9(1)

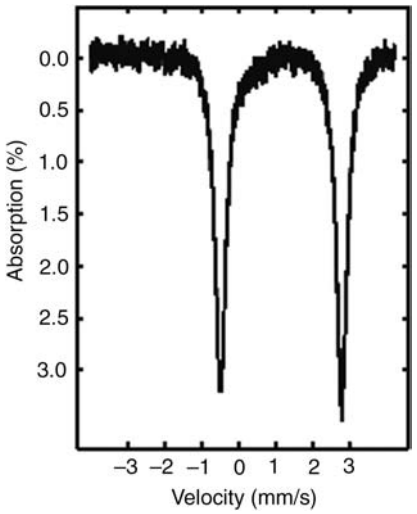

Figure 3. The Mössbauer spectrum of $[Fe(phppt)_2(SeCN)_2]\cdot 1.5MeOH$ (**4**·1.5MeOH) recorded at 5.2 K. The spectrum was recorded as a sucrose blend of the crystalline material.

Experimental

General

Elemental analyses (C, H, N and S) were carried out in the Campbell Microanalytical Laboratory, University of Otago, and have a standard error of ±0.3%. IR spectra were recorded on a Bruker ATR-IR spectrometer. All ^1H NMR spectra were recorded at 298 K on a Varian 400 MHz Inova NMR spectrometer using solvent residual peaks as a reference (chloroform $\delta = 7.260$ ppm (*22*)). The assignments are based on the atom-labelling scheme used in the X-ray crystal structures. ESI mass spectrometry was carried out on a Bruker micrOTOF$_Q$ mass spectrometer.

^{57}Fe Mössbauer spectra were also recorded at the University of Otago. Approximately, 10 mg of sample was ground together with crystalline sucrose and placed in a nylon sample holder (12.8-mm diameter, 1.6-mm thickness) with Kapton windows. Mössbauer spectra were measured on a Mössbauer spectrometer from Science Engineering & Education Co. (SEE Co., Edina, MN, USA) equipped with a closed cycle refrigerator system from Janis Research Co., Wilmington, MA, USA and Sumitomo Heavy Industries Ltd., Nishitokyo-City, Tokyo, Japan. Data were collected in constant acceleration mode in transmission geometry with an applied field of 47 mT parallel to the γ-rays. The zero velocity of the Mössbauer spectra refers to the centroid of the room temperature spectrum of a 25 μm metallic iron foil. Analysis of the spectra was carried out using the WMOSS program (SEE Co., formerly WEB Research Co).

Both complexations were carried out under argon using standard Schlenk conditions. All solvents and reagents were of reagent grade and used received unless otherwise stated, with the exception of methanol which was HPLC grade and ethanol which was distilled from Mg/I_2. $[Fe(py)_4(SCN)_2]$ and $[Fe(py)_4(SeCN)_2]$ were prepared from $[Fe(H_2O)_6](BF_4)_2$ according to the literature (*23*). N-phenyl-pyridine-2-thiocarboxamide and benzohydrazide were prepared as previously reported (*5*, *8*).

Ethyl N-phenylpyridine-2-carboximidothiate

A solution of sodium ethanoate was prepared by dissolving sodium (437 mg, 19 mmol) in distilled ethanol. The resulting colourless solution was stirred for 30 min, and then N-phenylpyridine-2-thiocarboxamide (4.06 g, 19 mmol) and ethyl bromide (3.60 g, 33 mmol) were added. The resulting orange solution was refluxed for 6 h during which time a white precipitate of NaBr formed. The mixture was filtered, and then the solvent was removed at reduced pressure to give a brown oil. This was dissolved in DCM (150 mL) and washed with distilled water (3 × 150 mL), saturated NaCl (50 mL) and saturated $NaHCO_3$ (50 mL) aqueous solutions. The orange DCM solution was then dried over $MgSO_4$, and the solvent was removed at reduced pressure to yield crude ethyl N-phenylpyridine-2-carboximidiothiate as a brown oil (4.55 g, 18.6 mmol, 98%). This crude material could be used in subsequent reactions without further purification and should be used promptly.

Phppt

An orange solution of freshly prepared ethyl N-phenylpyridine-2-carboximidothiate (2.0 g, 8.1 mmol) and benzohydrazide (1.35 g, 8.9 mmol) was refluxed in BuOH (50 mL) for 36 h. The resulting orange solution was allowed to cool to room temperature, resulting in the formation of some white precipitate. It was further cooled in the freezer before filtering off the solid and washing it with Et_2O (5 mL). The crude product (985 mg, 3.30 mmol, 41%) was recrystallised from hot MeOH (40 mL). After cooling in the freezer, the resulting white crystalline solid was isolated by vacuum filtration, washed with MeOH (5 mL) and dried in vacuo (795 mg, 2.66 mmol, 33% overall).

Found: C, 76.20; H, 4.74; N, 19.08 Calcd. for $C_{19}H_{14}N_4$ C, 76.49; H, 4.73; N, 18.78%. ^1H NMR (400 MHz, $CDCl_3$) 8.33 (1H, ddd, $J_{H3\text{-}H4} = 5$ Hz, $J_{H3\text{-}H5} = 2$ Hz, $J_{H3\text{-}H6} = 1$ Hz, pyH_3), 8.11 (1H, dt, $J_{H6\text{-}H5} = 8$ Hz, $J_{H6\text{-}H4} = J_{H6\text{-}}$

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$_{H3} = 1$ Hz, pyH_6), 7.75 (1H, td, $J_{H4\text{-}H3} = J_{H4\text{-}H5} = 8$ Hz, $J_{H4\text{-}H6} = 2$ Hz, pyH_4), 7.20–7.46 (11H, m, pyH_5, $2 \times phH_{2\text{-}6}$) ppm. ATR-IR $\nu/cm^{-1} = 1582$ (m), 1496 (m), 1469 (m), 1444 (m), 1425 (m), 801 (m), 771 (m), 715 (s), 601 (m). ESI-MS (pos.) *m/z*: $[Na(phppt)]^+$ (expected, 321.1116; found, 321.1104).

[Fe(phppt)$_2$(SCN)$_2$]·2MeOH (3·2MeOH)

Under argon, to a pale yellow solution of phppt (100 mg, 0.335 mmol) in 4:1 MeOH/$CHCl_3$ (40 mL) was added a pale yellow solution of $[Fe(py)_4(SCN)_2]$ (78 mg, 0.16 mmol) in MeOH (5 mL) causing the solution to turn deep red. After stirring for 1 h at room temperature, the resulting red solution was subjected to Et_2O vapour diffusion (still under argon), resulting in the formation of pale orange crystals suitable for X-ray diffraction. These were filtered off and dried under a flow of N_2 (30.8 mg, 0.040 mmol, 25%).

Found: C, 60.42; H, 4.12; N, 16.82; S, 7.55 Calcd. for $C_{40}H_{28}N_{10}S_2Fe$·2MeOH C, 60.58; H, 4.36; N, 17.20; S, 7.70% ATR-IR $\nu/cm^{-1} = 2052$ (s), 2028 (s), 1602 (w), 1495 (m), 1470 (s), 1435 (m), 1024 (w), 792 (s), 727 (m), 691 (s), 612 (w). ESI-MS (pos.) *m/z*: $[Fe(phppt)_2(SCN)]^+$ (expected, 710.1538; found, 710.1463), $[Na(phppt)_2]^+$ (expected, 619.2335; found, 619.2290), $[Na(phppt)]^+$ (expected, 321.1116; found, 321.1076).

[Fe(phppt)$_2$(SeCN)$_2$]·1.5MeOH (4·1.5MeOH)

Under argon, to a pale yellow solution of phppt (100 mg, 0.335 mmol) in 4:1 MeOH/$CHCl_3$ (40 mL) was added solid $[Fe(py)_4(SeCN)_2]$ (96.7 mg, 0.168 mmol), causing the solution to turn deep red as the solid dissolved. After stirring for 20 min at room temperature, the resulting deep red solution was subjected to Et_2O vapour diffusion (still under argon), resulting in the formation of a few orange crystals of $[Fe(phppt)_2(SeCN)_2]\cdot Et_2O$ suitable for X-ray diffraction and orange microcrystals. These were collected by filtration and dried under a flow of $N_{2(g)}$ to give $[Fe(phppt)_2(SeCN)_2]$·1.5-MeOH (56 mg, 0.0634 mmol, 38%).

Found: C, 54.94; H, 3.73; N, 15.19 Calcd. For $C_{40}H_{28}N_{10}Se_2Fe$·1.5MeOH: C, 54.74; H, 3.76; N, 15.38%. ATR-IR $\nu/cm^{-1} = 2056$ (s), 1602 (w), 1495 (m), 1470 (m), 1434 (m), 791 (s), 728 (m), 691 (s), 612 (m). ESI-MS (pos.) *m/z*: $[Fe(phppt)_2(SeCN)]^+$ (expected, 758.0982; found, 758.0935).

X-ray crystallography

X-ray crystallography was carried out on a Bruker Apex Kappa II area detector, using graphite–monochromatic Mo–Kα radiation ($\lambda = 0.710730(9)$ Å). The data were corrected for Lorentz and polarisation effects and semi-empirical absorptions corrections (SCALE) were applied. The structures were solved by direct methods (SHELXS-97) (*24*, *25*) and refined against all F^2 data (SHELXL-97) (*26*, *27*). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions and rode on the atoms to which they were attached with U(H) = 1.2U(non-H). CCDC 869782 & 869783.

[Fe(phppt)$_2$(SCN)$_2$]·2MeOH

$C_{42}H_{36}FeN_{10}O_2S_2$ (**3**·2MeOH), $M = 832.78$ g mol^{-1}, triclinic, $a = 8.9230(17)$ Å, $b = 9.5562(19)$ Å, $c = 13.421(2)$ Å, $\alpha = 95.117(10)°$, $\beta = 108.385(10)°$, $\gamma = 111.310(9)°$, $V = 984.5(3)$ Å^3, $T = 89(2)$ K, space group P-1, $Z = 1$, 14,321 reflections measured, 3832 unique ($R_{int} = 0.0553$) which were used in all calculations. Final w$R_2 = 0.1123$ (all data), $R_1 = 0.0453$ ($I > 2\sigma$).

[Fe(phppt)$_2$(SeCN)$_2$]·Et$_2$O

$C_{44}H_{38}FeN_{10}OSe_2$ (**4**·Et_2O), $M = 936.61$ g mol^{-1}, triclinic, $a = 8.9147(3)$ Å, $b = 10.0514(5)$ Å, $c = 13.2605(5)$ Å, $\alpha = 73.230(2)°$, $\beta = 70.767(2)°$, $\gamma = 67.756(2)°$, $V = 1019.99(7)$ Å^3, $T = 90(2)$ K, space group P-1, $Z = 1$, 12,338 reflections measured, 4176 unique (R_{int} 0.0404) which were used in calculations. Final w$R_2 = 0.0858$ (all data) and $R_1 = 0.0428$ ($I > 2\sigma$).

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