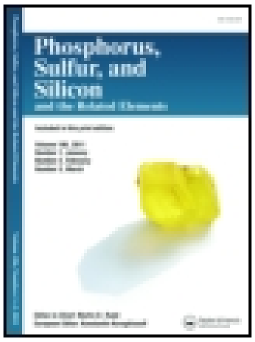

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Synthesis, crystal structures and magnetic properties of two iron (II) tris(pyridyl)phosphine selenides complexes

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Abstract: We reported the synthesis of tris(pyridyl)phosphine selenide (**TppSe**) and tris(4-methylpyridin-2-yl)phosphine selenide (**MeTppSe**), which were prepared by a simple and straightforward one-pot method with red phosphorus in a KOH/DMSO suspension, and treatment of resulted phosphines with selenium in hot toluene. These compounds were characterized by mass spectroscopy, ^{1}H, ^{13}C and ^{31}P NMR spectroscopies and the structure of **MeTppSe** was characterised by a single-crystal X-ray diffraction. Furthermore, The reactions of selenides with $Fe(ClO_4)_2\cdot6H_2O$ afforded two new iron(II) mononuclear metal complexes $[Fe(TppSe)_2][ClO_4]_2\cdot3DMF$ (**1**) and $[Fe(MeTppSe)_2][ClO_4]_2\cdot2DMF$ (**2**). Detailed structural analyses and magnetic susceptibility measurements confirm no spin transition from low-spin to the high-spin state between 2 and 300 K in two iron(II) complexes.

Introduction

Over the last decade, organophosphorus compounds and their chalcogenides derivatives attracted much attention because of their unique chemical and physical properties and their applications in a variety of advanced materials.[1-3] Among them, pyridyl-substituted phosphines have been extensively used in metal ion coordination chemistry for their ease of functionalization and the electronic properties that they impart to metal complexes used for catalysis purposes. Tris(2-pyridyl)phosphine exhibits rich coordination capabilities, forming a variety of complexes owing to its high-performance group combining molecular flexibility, and a large number of metal complexes have been found, in which the pyridylphosphines ligands bind to the metal.[4-11] On the other hand, the coordination chemistry of tris(2-pyridyl)phosphine chalcogenides is poorly investigated, and only several example based on tris(2-pyridyl)phosphine selenide have been prepared.[5] However, to the best of our knowledge, no study about iron (II) complex has been reported so far based on the tris(2-pyridyl)phosphine selenide ligands.

On the other hand, magnetic bistability induced by external stimuli (such as temperature, pressure, magnetic field or light) has attracted much attention because of their potential technological applications. We recently synthesized a cyano-bridged $\{Fe_2Co_2\}$ grid and two mixed-valence $\{Fe^{III}_2Fe^{II}_2\}$ clusters, which exhibited reversible thermally intramolecular charge transfer induced spin transition (CTIST) and spin crossover (SCO) properties, respectively.[12, 13] According to the relevant literature, we find that substituted tris(pyrazolyl)borate and tris(pyrazolyl)methane ligands induce a variety of electronic spin-state behaviors in iron complexes,[14-16] which led us to undertake an extensive investigation of the iron (II) complexes formed with other tripodal ligands. Herein, we report the first iron(II) mononuclear metal complexes with tris(pyridyl)phosphine selenide and thoroughly characterize them by single-crystal X-ray diffraction and magnetic susceptibility measurements.

Result and discussion

Synthesis

Two tris(pyridyl)phosphine ligands are synthesized by the reaction of 2-bromopyridine or 2-bromo-4-methylpyridine with red phosphorus in a superbasic KOH/DMSO(H_2O) suspension at 120 °C for 1 h to afford tris(2-pyridyl) phosphine (**Tpp**) and tris(4-methylpyridin-2-yl)phosphine (**MeTpp**). [9, 17, 18] Two phosphines are easily oxidized by treatment of appropriate phosphine with elemental selenium in refluxing toluene to afford the corresponding phosphine chalcogenides **TppSe** and **MeTppSe**, [10, 19] and the identity of **MeTppSe, 1** and **2** were also confirmed crystallographically. The synthesis of two metal complexes **1** and **2** are performed by reaction of 2 equiv of **TppSe** or **MeTppSe** with the appropriate $Fe(ClO_4)_2{\cdot}6H_2O$ salt in DMF under an N_2 atmosphere in good yields (Scheme 1). The mass spectra of complexes **1** and **2** in CH_3OH (Figure S3 and S4) show strong peaks at m/z = 373.14, and 414.73, for $[Fe(TppSe)_2]^{2+}$ and $[Fe(MeTppSe)_2]^{2+}$, respectively, indicating that two iron(II) mononuclear metal complexes are stable in solution.

NMR spectral studies

^1H NMR, ^{13}C NMR and ^{31}P NMR spectra of **Tpp, TppSe, MeTpp** and **MeTppSe** are given in the supplemental materials. The comparison of the ^1H NMR spectra for phosphines and selenides reveals that the selenium atom does not obviously effect on δ_H values. However, some of C resonance on pyridine split into doublets indicating that there exist the P-C couplings based on ^{13}C NMR spectra of four ligands (see below experimental part and supplemental materials).

The coupling constants of $^{1}J_{C,P}$ in phosphines ligands are significantly different comparing with selenides ligands. The $^{1}J_{C,P}$ value in selenides ligands (105.6 Hz in **TppSe** and 105.3 Hz in **MeTppSe**) are larger than those of phosphines ligands ($^{1}J_{C,P}$ = 12.1 Hz in **Tpp** and **MeTpp**). Phosphorus with different chemical valence (tervalence in phosphines ligands and pentavalence in selenides ligands) has different effects on P-C coupling constants.[20] Furthermore, the resonance in the ^{31}P NMR spectra of **Tpp, MeTpp** and **TppSe, MeTppSe** appears at –0.78, -0.35 and 28.97, 29.00 ppm, respectively, and the δ_P values of selenides ligands are also larger than those of phosphines ligands. These chemical shifts are similar to the related phosphines and selenides that were previously reported in the literature. [9, 19]

Single crystal X-ray studies

Details of the crystal data and structure refinement parameters for **MeTppSe**, **1** and **2** are summarized in Table 1. Selected bond distances and angles are included in Table 2. ORTEP of **MeTppSe** is presented in Figure 1, and the asymmetric unit (Monoclinic, $P2_1$/n) contains two independent molecules. In two molecules, the nitrogen atoms (N2, N3 and N5, N6) point to the opposite direction as the selenium atoms (Se1 and Se2), respectively, while the remaining nitrogen atoms (N1 and N4) point in the same direction. This type of arrangement has been previously seen in the structure of tris(2-pyridyl)phophine oxide and tris(2-pyridyl)phophine sulphide. However, in the reported tris(2-pyridyl)phophine selenide structure, [19] all nitrogen atoms point in the same direction as the Se atom, which can be related to the steric requirement in the structure of **MeTppSe** bearing a methyl group at the 4-position of the pyridyl ring. The P-Se bond distances, 2.1043(13) Å and 2.1066(14) Å, are comparable with similar structures found in the literature showing typical double bond character.[19]

The molecular structures of complexes **1** and **2** are determined by X-ray crystallography at 296 K and 100 K, respectively. Complex **1** and **2** crystallize in the Monoclinic space group $P2_1$ and triclinic space group *P*-1 with three DMF molecules in **1** and two DMF molecules in **2**, respectively. As shown in Figure 2, the crystal structures of **1** and **2** are similar. **TppSe** and **MeTppSe** act as tripodal ligands, and the Fe^{II} atoms lie on an inversion center and are octahedrally coordinated by the N atoms of two tridentate ligands with expected six-coordinate geometry. The three pyridine planes of each ligand are parallel to the P-Fe-P axis.

It should be noted that the coordination bond lengths in **1** (av. 2.008 Å) and **2** (av. 2.004 Å) (Table 1) are slightly longer than those of the $[Fe\{N(py)_3\}_2]^{2+}$ (1.982 Å), $[Fe\{CH(py)_3\}_2]^{2+}$ (1.949 Å), $[Fe\{CH_3C(py)_3\}_2]^{2+}$ (1.973 Å) and $[Fe(TppO)_2)_2]^{2+}$ (1.982 Å) [22, 22, 23], but similar with other reported average $[Fe\text{-}N(py)_6]^{2+}$ bond lengths in $[Fe(TppO)_2]^{2+}$ based on tris(2-pyridyl)phosphine oxide ligand. [24] In addition, the distortion parameter values Σ of geometries around Fe^{II} ions are 20.2° for **1** and 19.9°, 19.3° for **2**, respectively. In general, high spin Fe^{II} ions tend to form more distorted octahedra and thus have larger Σ values than their low spin counterparts. According to above analysis, we can infer that the spin state of Fe^{II} ion in **1** and **2** is the LS state, which is in accordance with the magnetic data (see below). The P=Se bond lengths in the Fe^{II} complexes (2.079 Å, 2.091 Å for **1** and 2.085 and 2.077 Å for **2**) are a litter shorter than those in the free **MeTppSe** ligand (2.103 Å and 2.106 Å), which are due to the strong effect of spin delocalization in **1** and **2.** Furthermore, the C–P–C angles of two Fe^{II} complexes lie in the range 100.7°–104.1°, comparable to 102.7°–107.8° Å in free **MeTppSe** ligand.

Magnetic properties

Magnetic susceptibility measurements in a 1000 Oe field were performed on **1** and **2** in the temperature range of 2–300 K, and are shown as $\chi_M T$ versus T plots (Figure 4). The $\chi_M T$ values of **1** and **2** do not change as the temperature increased from 30 K to 300 K, which shows a great tendency to stabilize the LS state with S = 0 and is very similar to that observed for related Fe^{II} complex systems chelating bis-tripodal ligands showing no temperature dependence (LS state) in the measuring temperature range. [21, 22] Although the coordination bond lengths in **1** and **2** are slightly longer than those of the $[Fe\{CH(py)_3\}_2]^{2+}$, $[Fe\{CH_3C(py)_3\}_2]^{2+}$ and $[Fe(TppO)_2)_2]^{2+}$ (See above), the magnetic moments on **1** and **2** show that they are fully low spin at room temperature, and the small differences noted in the Fe–N distances (Table 4) cannot be correlated with any differences in magnetic properties, which can be found in some of the similar $[Fe\text{-}N(py)_6]^{2+}$ compounds with such same phenomenon. In general, Fe^{II} complexes exist in either a high spin or a low spin state, depending on the nature of the ligand field on the metal ions. We devote ourselves to select and change the ligands with different electron-donating groups in order to get intermediate ligand field, but spin transition from low-spin to the high-spin state is not detected between 2 and 300 K in two complexes.

Conclusions

In summary, we report a simple and straightforward one-pot method for the synthesis of tris(2-pyridyl)phosphines with red phosphorus in a KOH/DMSO suspension. Moreover, two iron(II) mononuclear metal complexes based on the tris(2-pyridyl)phosphine selenide ligands in a N,N',N''-tripodal mode have been successfully synthesized. Based on the detailed structural analyses and magnetic susceptibility measurements, no spin transition happened from low-spin to the high-spin state between 2 and 300 K in two iron(II) complexes. We think that our result for synthesizing two new iron(II) mononuclear metal complexes will have some impact for the preparation of novel SCO molecular materials. Further studies on the fabrication of new iron(II) metal complexes are ongoing.

Experimental

Materials and methods

All chemicals were commercial and purified according to standard procedures. All organic solvents were dried and freshly distilled before use. The ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Bruker AV 300 MHz and 400 MHz spectrometers using $CDCl_3$ as the solvent. Chemical shifts are given with respect to tetramethylsilane (^{1}H, ^{13}C) and phosphoric acid (^{31}P) and ^{31}P spectra were calibrated externally and chemical shifts are expressed in δ (ppm). Mass spectra were measured on a LCQ Advantage MAX (ESI). The melting points of the synthesized compounds were recorded on a WRX-4 monocular microscope and were not corrected. Magnetic susceptibility measurement was carried out on a Quantum Design MPMS SQUID-VSM magnetometer in the temperature range of 2−300 K with a magnetic field of 2000 Oe and the magnetic susceptibilities of the two complexes were measured at a sweep rate of 3 K min^{-1}. Magnetic data were calibrated with the sample holder and diamagnetic contributions. The Supplemental Materials contains sample ^{1}H, ^{13}C, ^{31}P NMR spectra and mass spectra for the products.

Structural Studies

Single crystal structural data for **MeTppSe**, **1** and **2** were collected on a Bruker Apex-II CCD diffractometer using graphite-collimated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXL97) and completed by difference Fourier methods

(SHELXL97).[25] Refinement was performed against F^2 by weighted full-matrix least-squares (SHELXL97) and empirical absorption corrections (SADABS) were applied.[26] Hydrogen atoms were found in difference maps and subsequently placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters.

CCDC 1575133, 1575137 and 1575138 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Preparation of tris(pyridyl)phosphine ligands Tpp and MeTpp.

A mixture of 2-bromopyridine (20 mmol) or 2-bromo-4-methylpyridine, red phosphorus (50 mmol), powdered KOH (60 mmol), DMSO (30 mL), and H_2O (1 mL) was stirred for 1 h at 120 ^oC under argon. The mixture was cooled to room temperature, diluted with H_2O (60 mL) and extracted with $CHCl_2$ (3 x 20 mL). The combined extract was washed with H_2O (3 x 20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue washed with diethyl ether (10 mL) and dried in vacuo to afford pure phosphine product as a microcrystalline powder.

Tris(2-pyridyl)phosphine **Tpp**: Yield: 1.52 g (86 %). m.p. 113 °C (lit.[19] 113 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm: 8.73 (d, 4.4 Hz, 3H), 7.61-7.66 (m, 3H), 7.43 (d, J = 7.7 Hz, 3H), 7.21-7.25 (m, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 122.8, 129.2 (d, $^2J_{C,P}$ = 19.5 Hz), 135.9 (d, $^3J_{C,P}$ = 3.9 Hz), 150.3 (d, $^1J_{C,P}$ = 12.1 Hz), 161.2 (d, $^3J_{C,P}$ = 2.8 Hz) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = -0.78 ppm. ESI-MS: m/z = 266.01 ($[M+H]^+$), 288.02 ($[M+Na]^+$), 552.92 ($[2M+Na]^+$). HRMS (ESI+, CH_3OH): m/z (%) = 266.0841 ($[M+H]^+$ requires 266.0842).

Tris(4-methylpyridin-2-yl)phosphine **MeTpp**: Yield: 1.68 g (82 %). m.p. 94 °C. MS (EI$^+$, 70 eV): *m/z* (%): 307 (6) [M]$^+$, 215 (100) [M-Py^{Me}]$^+$, 200 (10) [M-Py^{Me}-Me]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm: 8.58 (t, *J* = 9.6 and 4.8 Hz, 3H), 7.30 (d, *J* = 9.6 Hz, 3H), 7.02 (d, *J* = 4.8 Hz, 3H), 2.28 (s, 9H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 21.1, 123.7, 130.1 (d, $^2J_{C,P}$ = 21.2 Hz), 146.9 (d, $^3J_{C,P}$ = 4.5 Hz), 150.1 (d, $^1J_{C,P}$ = 12.1 Hz), 161.2 (d, $^3J_{C,P}$ = 3.3 Hz) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = -0.35 ppm. ESI-MS: m/z = 308.16 ([M+H]$^+$), 330.15 ([M+Na]$^+$), 637.05 ([2M+Na]$^+$). HRMS (ESI+, CH_3OH): m/z (%) = 308.1311 ([M+H]$^+$ requires 326.1311).

Preparation of tris(pyridyl)phosphine selenide **ligands TppSe and MeTppSe.**

To a solution of **Tpp** or **MeTpp** (10 mmol) in degassed toluene (20 ml), powdered gray selenium (14 mmol) was added and the suspension was refluxed for 10 h. After cooling to room temperature the suspension was filtered via a syringe filter and the filtrate is evaporated to dryness under vacuum. The crude product was washed with ethanol (20 mL). After drying in vacuo a beige-colored powder was obtained.

Tris(2-pyridyl)phosphine selenide **TppSe**: Yield: 3.1 g (90 %). m.p. 176 °C (lit.[19] 176-178 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.72 (d, *J* = 4.5 Hz, 3H), 8.34 (t, *J* = 7.4 Hz, 3H), 7.78-7.85 (m, 3H), 7.32-7.37 (m, 3H), ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 125.1 (d, $^4J_{C,P}$ = 2.9 Hz), 129.4 (d, $^2J_{C,P}$ = 26.1 Hz), 136.4 (d, $^3J_{C,P}$ = 10.6 Hz), 150.0 (d, $^3J_{C,P}$ =18.9 Hz), 154.2 (d, $^1J_{C,P}$ =105.6 Hz) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 28.97 ppm. ESI-MS: m/z = 345.86 ([M+H]$^+$), 712.62 ([2M+Na]$^+$). HRMS (ESI+, CH_3OH): m/z (%) = 346.0005 ([M+H]$^+$ requires 346.0007).

Tris(4-methylpyridin-2-yl)phosphine selenide **MeTppSe**: Yield: 3.3 g (86 %). m.p. 167-168 °C. MS (EI$^+$, 70 eV): *m/z* (%): 387 (18) [M]$^+$, 306 (15) [M-Se]$^+$, 215 (100) [M-SePy^{Me}]$^+$, 200

(13) [M-SePy^{Me}-Me]$^+$, 92 (6) [Py^{Me}]$^+$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.57 (d, J = 4.8 Hz, 3H), 8.14 (d, J = 7.2 Hz, 3H), 7.14 (d, J = 4.8 Hz, 3H), 2.39 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 21.2 (d, $^4J_{C,P}$ = 1.3 Hz), 125.8 (d, $^4J_{C,P}$ = 3.2 Hz), 130.1 (d, $^2J_{C,P}$ = 26.2 Hz), 147.7 (d, $^3J_{C,P}$ = 10.6 Hz), 149.8 (d, $^3J_{C,P}$ =19.8 Hz), 154.3 (d, $^1J_{C,P}$ =105.3 Hz) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.00 ppm. ESI-MS: m/z = 388.02 ([M+H]$^+$). HRMS (ESI+, CH_3OH): m/z (%) = 388.0472 ([M+H]$^+$ requires 388.0476).

Preparation of [Fe(TppSe)$_2$][ClO$_4$]$_2$·3DMF (1)and [Fe(MeTppSe)$_2$][ClO$_4$]$_2$·2DMF (2)

Under an argon atmosphere, A solution of $Fe(ClO_4)_2\cdot6H_2O$ (0.1 mmol) and **TppSe** or **MeTppSe** (0.2 mmol) in DMF (4 mL) was stirred at room temperature for 2 h and left it under the diffusion of diethyl ether vapor slowly without disturbance. Dark-red blocks crystals suitable for X-ray structure analysis were obtained and isolated *via* filtration after about 3 d.

[Fe(TppSe)$_2$][ClO$_4$]$_2$·3DMF 1: Yield: 95 mg (82 %). ESI-MS: [M]$^{2+}$ calculated for [Fe(TppSe)$_2$]$^{2+}$: 372.96; Found: 373.14. Elemental analysis (%) calculated for $C_{39}H_{45}Cl_2N_9O_{11}P_2Se_2Fe$: C 40.30, H 3.90, N 10.84; Found: C 40.25, H 4.08, N 10.65.

[Fe(MeTppSe)$_2$][ClO$_4$]$_2$·2DMF 2: Yield: 94 mg (80 %). ESI-MS: [M]$^{2+}$ calculated for [Fe(MeTppSe)$_2$]$^{2+}$: 415.00; Found: 414.73. Elemental analysis (%) calculated for $C_{42}H_{50}Cl_2N_8O_{10}P_2Se_2Fe$: C 42.99, H 4.29, N 9.55; Found: C 42.89, H 4.35, N 9.51.

Funding

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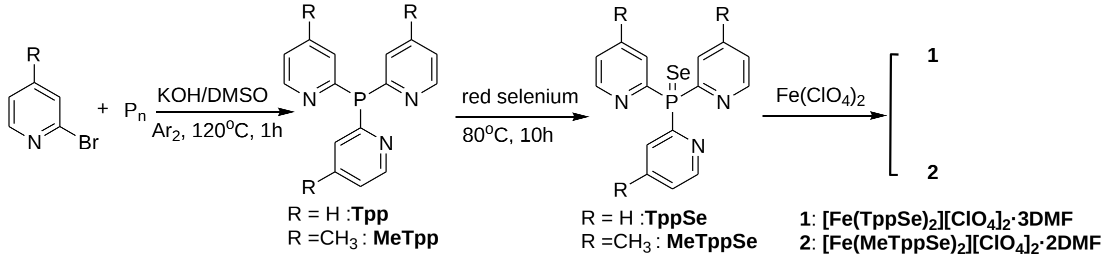

Scheme 1 Synthetic procedure for two metal complexes **1** and **2**

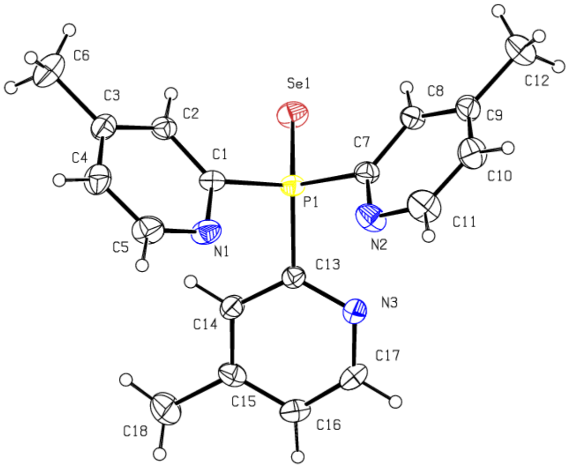

Figure 1. Molecular structure of **MeTppSe**

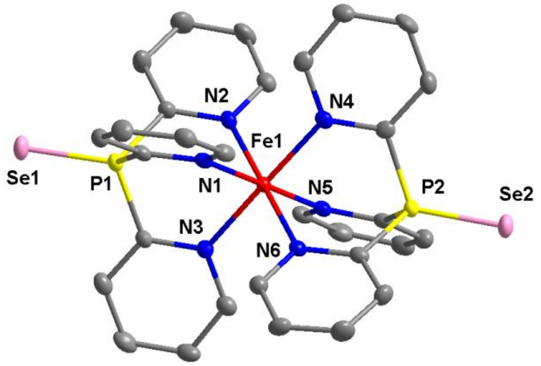

Figure 2. Molecular structure of the **1**, anions, solvent molecules, and hydrogen atoms are omitted for clarity

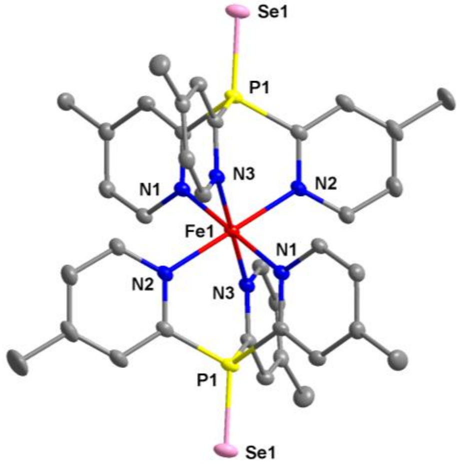

Figure 3. Molecular structure of the **2**, anions, solvent molecules, and hydrogen atoms are omitted for clarity

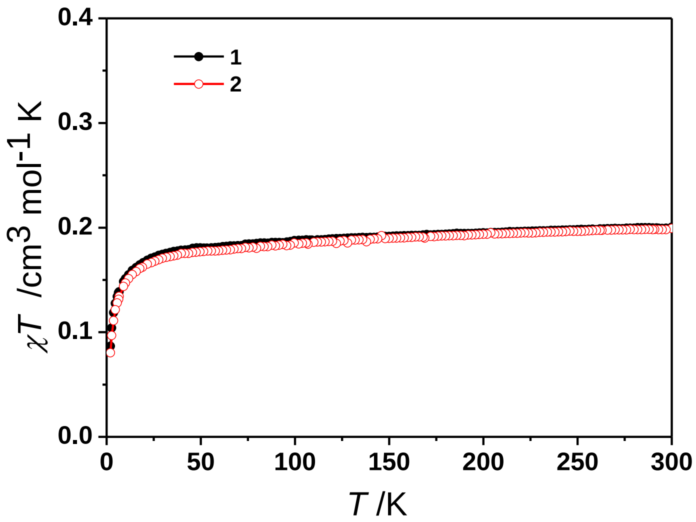

Figure 4. Temperature dependence of $\chi_M T$ plots for **1** and **2**

Table 1. Crystal structure and data refinement parameters for compounds **MeTppSe**, **1** and **2**

Compound	**MeTppSe**	**1**	**2**
Temperature / K	298	100	298
Formula	$C_{18}H_{18}N_3PSe$	$C_{39}H_{45}Cl_2N_9O_{11}P_2Se_2Fe$	$C_{42}H_{50}Cl_2N_8O_{10}P_2Se_2Fe$
Formula weight	386.28	1162.45	1173.51
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1$	P-1
a /Å	14.154(3)	11.5861(14)	12.1451(12)
b /Å	8.4907(19)	17.224(2)	13.2797(13)
c /Å	30.189(7)	12.2355(15)	16.5383(16)
α /°	90	90	79.689(2)
β /°	97.841(4)	110.213(2)	73.4610(10)
γ /°	90	90	86.613(2)

V / Å^3	3594.0(14)	2291.3(5)	2515.6(4)
Z	8	2	2
D calcd/g cm^{-3}	1.428	1.685	1.549
μ / mm^{-1}	2.181	2.173	1.978
Collected reflections	18180	15606	23174
Unique reflections	7032	8671	8803
Data / restraints / parameters	7032 / 0 / 421	8671 / 37 / 629	8803 / 84 / 696
GOF on F^2	1.131	1.081	1.072
Final R indices [I >2σ (I)]	R_1 = 0.0547	R_1 = 0.0289	R_1 = 0.0399
	wR_2 = 0.1438	wR_2 = 0.0796	wR_2 = 0.1178
R indices (all data)	R_1 = 0.0720	R_1 = 0.0307	R_1 = 0.0519
	wR_2 = 0.1507	wR_2 = 0.0806	wR_2 = 0.1374

Table 2. Selected bond distances (Å), angles (°) and structural parameters in these complexes

compound	**P=Se (Å)**	**C–P–C (°)**	**Fe–N$_{Average}$ (Å)**	**$\Sigma_{Fe}{}^{a}$**
TppSe^b	2.1050(15)	104.76(13); 104.76(13); 104.76(13)		
MeTppSe	2.1043(13)	107.8(2); 102.7(2); 106.3(2)		
	2.1066(14)	106.6(2); 105.7(2); 103.6(2)		
1	2.0787(9)	102.96(14); 101.70(14); 104.02(15)	2.008(3)	20.2
	2.0907(9)	103.63(15); 103.59(14); 101.09(14)		
2	2.0851(9)	103.82(17); 100.69(16); 103.52(16)	2.004(3)	19.9
	2.0773(10)	103.39(15); 102.91(15); 102.54(15)	2.004(3)	19.3

$\Sigma_{Fe}{}^{a}$: the sum of the deviation from 90° of the 12 cis-angles of the FeN$_6$ octahedron; TppSe^b: Crystallographic data is obtained from CCDC number 720507.