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

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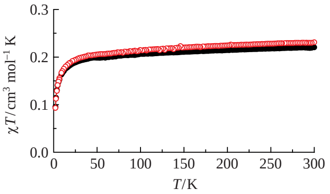
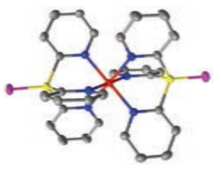
Two iron(II) mononuclear metal complexes with tris(pyridyl)-phosphine sulfides and $Fe(ClO_4)_2 \cdot 6H_2O$ have been synthesized and characterized. Detailed structural analyses and magnetic susceptibility measurements confirm no spin transition from low-spin to the high-spin state between 2 and 300 K in these complexes.





Pyridylphosphine ligands and their chalcogenide derivatives are of considerable interest due to their fundamental importance and prospective applications.[1–3] Tris(2-pyridyl)phosphine exhibits rich coordination capabilities owing to its unique structure, and a large number of metal complexes with pyridylphosphine ligands are reported;[4–12] however, the coordination chemistry of tris(2-pyridyl)-phosphine chalcogenides is poorly known.[5]

Magnetic bistability induced by external stimuli (such as temperature and light) attracts much attention. 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 and spin crossover properties, respectively.[13,14] The fact that substituted tris(pyrazolyl)borate and tris(pyrazolyl)methane ligands induce a variety of electronic spin-state behaviors in iron complexes[15–17] led us to undertake an extensive investigation into the iron(II) complexes formed with other tripodal ligands. Herein, we report the first iron(II) mononuclear complexes with tris(pyridyl)phosphine chalcogenides and thoroughly characterize them by single-crystal X-ray diffraction and magnetic susceptibility measurements.

Two tris(pyridyl)phosphine ligands were synthesized by a 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) or tris(4-methylpyridin-2-yl)phosphine (MeTpp).[10,18,19] These phosphines are easily oxidized by treatment with elemental sulfur in refluxing toluene to give corresponding phosphine chalcogenides (TppS and MeTppS).[20] The identity of MeTpp or MeTppS† was also confirmed crystallographically (Figure 1).

The synthesis of complexes **1** and **2** was performed by a reaction of two equivalents of TppS or MeTppS with $Fe(ClO_4)_2 \cdot 6H_2O$, in DMF or MeCN under an N_2 atmosphere in good yields.‡ The molecular structures of complexes **1** and **2** were determined by X-ray crystallography at 296 and 100 K, respectively (Figure 2).§ Complexes **1** and **2** crystallize in the triclinic space group $P\bar{1}$ with two DMF molecules in **1** and six MeCN molecules in **2**. TppS or MeTppS acts as a tripodal ligand, and the Fe^{II} atom lies on an inversion center and is octahedrally coordinated by the N atoms of two tridentate ligands with an expected six-coordinate geometry.

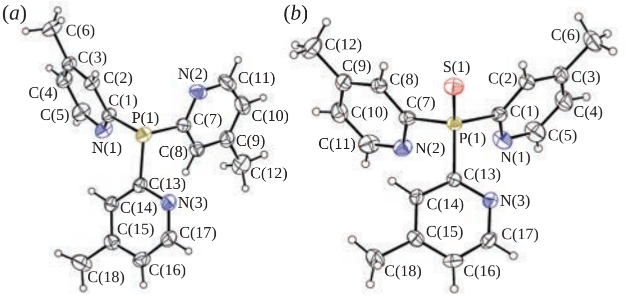


Figure 1 Molecular structure of (*a*) MeTpp and (*b*) MeTppS.

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† *Tris(4-methylpyridin-2-yl)phosphine* (*MeTpp*): ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.58 (t, 3H, *J* 9.6 and 4.8 Hz), 7.30 (d, 3H, *J* 9.6 Hz), 7.02 (d, 3H, *J* 4.8 Hz), 2.28 (s, 9H). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ: 21.1, 123.7, 130.1 (d, J_{CP} 21 Hz), 146.9 (d, J_{CP} 4.5 Hz), 150.1 (d, J_{CP} 12 Hz), 161.2 (d, J_{CP} 3 Hz). MS (EI$^+$, 70 eV), *m/z* (%): 307 (6) [M]$^+$, 215 (100) [M–Py^{Me}]$^+$, 200 (10) [M–Py^{Me}–Me]$^+$.

Tris(4-methylpyridin-2-yl)phosphine sulfide (MeTppS): ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.60 (d, 3 H, J_2 4.8 Hz), 8.12 (d, 3H, *J* 7.2 Hz), 7.17 (d, 3H, *J* 4.8 Hz), 2.39 (s, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 21.2, 125.9 (d, J_{CP} 3.1 Hz), 129.5 (d, J_{CP} 24.9 Hz), 147.6 (d, J_{CP} 10.4 Hz), 149.3 (d, J_{CP} 19.9 Hz), 154.8 (d, J_{CP} 113.4 Hz). MS (ESI), *m/z*: 340.07 [M+H]$^+$. MS (EI$^+$, 70 eV), *m/z*, (%): 339 (18) [M]$^+$, 306 (54) [M–S]$^+$, 247 (41) [M–Py^{Me}]$^+$, 215 (100) [M–SPy^{Me}]$^+$, 92 (10) [PyMe]$^+$.

‡ *Synthesis of* $[Fe(TppS)_2][ClO_4]_2 \cdot 2DMF$ **1**. Under an argon atmosphere, a solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.036 g, 0.1 mmol) and TppS (0.060 mg, 0.2 mmol) in DMF (4 ml) was stirred at room temperature for 2 h and left under the diffusion of diethyl ether vapor slowly without disturbance. Dark-red block crystals suitable for X-ray structure analysis were obtained and isolated by filtration after about three days. Yield, 0.070 g.

Synthesis of $[Fe(MeTppS)_2][ClO_4]_2 \cdot 6MeCN$ **2**. Under an argon atmosphere, solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.036 g, 0.1 mmol) and MeTppS (0.068 mg, 0.2 mmol) in MeCN (5 ml) was stirred at room temperature for 2 h and left it under the diffusion of diethyl ether vapor slowly without disturbance. Dark-red block crystals suitable for X-ray structure analysis were obtained and isolated by filtration after about five days. Yield, 0.065 g.

Table 1 Selected bond distances, angles and structural parameters.

Compound	P=X/Å	C–P–C/deg	Fe–N$_{average}$/Å	Σ_{Fe}^{a}
MeTpp		100.06(7), 105.14(7), 96.19(7)		
MeTppS	1.9506(16)	107.53(19), 105.8(2), 103.16(19)		
	1.9507(16)	106.49(19), 104.17(19), 105.4(2)		
1	1.9283(14)	102.62(18), 104.78(17), 101.68(17)	2.009(3)	21.5
	1.9268(12)	104.45(15), 101.43(15), 102.74(15)	2.017(3)	17.6
2	1.9348(6)	103.61(7), 102.80(7), 103.11(7)	2.0150(14)	18.7

$^a\Sigma_{Fe}$ is the sum of the deviation from 90° of the 12 *cis*-angles of the FeN_6 octahedron.

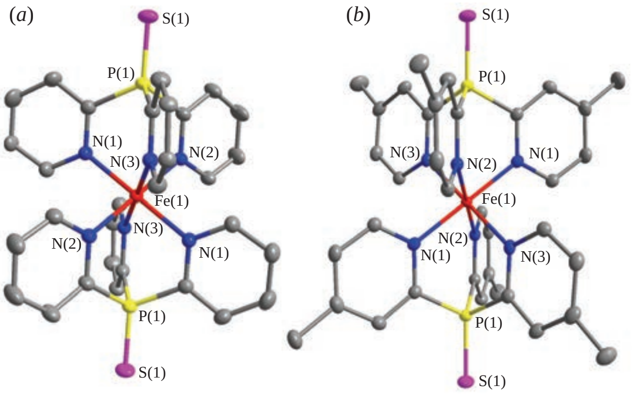

Figure 2 Molecular structure of complexes (*a*) **1** and (*b*) **2**. Anions, solvent molecules and hydrogen atoms are omitted for clarity.

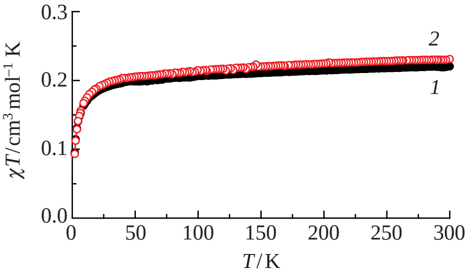

Figure 3 Temperature dependence of $\chi_M T$ plots for complexes (*1*) **1** and (*2*) **2**.

Note that the coordination bond lengths in **1** (av. 2.01 Å) and **2** (av. 2.02 Å) (Table 1, Figure 2) 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), $\{Fe[MeC(py)_3]_2\}^{2+}$ (1.973 Å) and $\{Fe[(TppO)_2]_2\}^{2+}$ (1.982 Å) based on a tris(2-pyridyl)phosphine oxide ligand.[21–23] In addition, the Σ values are 21.5 and 17.6° for **1** or 18.7° for **2**. Thus, the spin state of the Fe^{II} ion in **1** and **2** is the LS state, which is in accordance with the magnetic data (see below). The P=X bond lengths in the Fe^{II} complexes (1.927 and 1.928 Å for **1** and 1.935 Å for **2**) are shorter than those in the free MeTppS ligand (1.951 Å), whereas the C–P–C angles of the complexes are 101.7–104.8°, comparable to 103.2–107.5° in the free MeTppS ligand.

Magnetic susceptibility measurements in a 1000 Oe field were performed in a temperature range of 2–300 K (Figure 3). The $\chi_M T$ values of **1** and **2** did not change as the temperature increased from 30 to 300 K to show a tendency to the LS state stabilization, which is very similar to that observed for related Fe^{II} complex systems chelating bis-tripodal ligands exhibiting no temperature dependence (LS state) in the test temperature range.[22,23] In addition, the $\chi_M T$ values of **1** and **2** are 0.20 cm^3 mol^{-1} K at 30 K, indicating that about 5% of iron(II) ions still remain in the high-spin states, with the non-zero value being due to second order Zeeman contributions from the t_{2g} configuration[6] possibly augmented by some remnant HS form.[15–17,24] This is in accordance with structure analysis (the coordination bond lengths in **1** and **2** are slightly longer than those of the $\{Fe[(TppO)_2]_2\}^{2+}$ (1.982 Å) based on the tris(2-pyridyl)phosphine oxide ligand). The decrease of $\chi_M T$ below 30 K is due to zero-field splitting.[15–17,25,26] 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, however spin transition from low-spin to the high-spin state is not detected between 2 and 300 K in two complexes.

In summary, two mononuclear iron(II) complexes with the tris(2-pyridyl)phosphine sulfide ligands in a N,N′,N″-tripodal mode have been successfully synthesized. Although a spin transition from low-spin to high-spin state was not detected at 2–300 K in the two complexes, we believe that our results will have some impact on the preparation of novel SCO molecular materials.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.034.

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§ *Crystal data for MeTpp*. $C_{18}H_{18}N_3P$, M = 307.32, monoclinic, space group $P2_1/n$, a = 11.1546(17), b = 12.1839(19) and c = 13.133(2) Å, β = 113.981(2)°, V = 1630.8(4) Å^3, Z = 4, d_{calc} = 1.252 g cm^{-3}, μ(MoKα) = = 0.753 mm^{-1}, T = 296(2) K, 17449 reflections measured, 4940 independent reflections (R_{int} = 0.0471), final R_1 = 0.0694 [$I > 2\sigma(I)$], wR_2 = 0.1567, GOF = 1.045.

Crystal data for MeTppS. $C_{18}H_{18}N_3PS$, M = 339.38, monoclinic, space group $P2_1/n$, a = 14.023(3), b = 8.4045(18) and c = 30.400(6) Å, β = 98.391(3)°, V = 3544.5(13) Å^3, Z = 8, d_{calc} = 1.272 g cm^{-3}, μ(MoKα) = = 0.275 mm^{-1}, T = 296(2) K, 25914 reflections measured, 6193 independent reflections (R_{int} = 0.0731), final R_1 = 0.0834 [$I > 2\sigma(I)$], wR_2 = 0.1897, GOF = 1.045.

Crystal data for **1**. $C_{35}H_{38}Cl_2N_8O_{10}P_2S_2Fe$, M = 983.54, triclinic, space group $P\bar{1}$, a = 12.4325(14), b = 12.9046(14) and c = 14.5901(16) Å, α = = 97.769(2)°, β = 105.062(2)°, γ = 92.435(2)°, V = 2232.2(4) Å^3, Z = 2, d_{calc} = 1.463 g cm^{-3}, μ(MoKα) = 0.684 mm^{-1}, T = 296(2) K, 22066 reflections measured, 8686 independent reflections (R_{int} = 0.0594), final R_1 = 0.0719 [$I > 2\sigma(I)$], wR_2 = 0.2073, GOF = 1.077.

Crystal data for **2**. $C_{48}H_{54}Cl_2N_{12}O_8P_2S_2Fe$, M = 983.54, triclinic, space group $P\bar{1}$, a = 11.2851(10), b = 11.5247(10) and c = 11.8662(11) Å, α = = 88.1050(10)°, β = 80.6610(10)°, γ = 64.3540(10)°, V = 1371.6(2) Å^3, Z = 1, d_{calc} = 1.428 cm^{-3}, μ(MoKα) = 0.569 mm^{-1}, T = 100(2) K, 15996 reflections measured, 6551 independent reflections (R_{int} = 0.0333), final R_1 = 0.0373 [$I > 2\sigma(I)$], wR_2 = 0.1070, GOF = 1.052.

CCDC 1568321, 1568322, 1568324 and 1568325 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.

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