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# $[Fe(4'-PhStpy)_2][PF_6]_2$ (4'-PhStpy = 4'-phenylthio-2,2':6',2"-terpyridine): A centrosymmetric embrace

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### ARTICLE INFO

## ABSTRACT

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Keywords: 4'-Phenylthio-2,2':6',2"-terpyridine Crystal structure Iron Host-guest The syntheses and characterizations of 4'-phenylthio-2,2':6',2"-terpyridine (4'-PhStpy) and  $[Fe(4'-PhStpy)_2]$ [PF<sub>6</sub>]<sub>2</sub> are reported. In the solid state, centrosymmetric pairs of  $[Fe(4'-PhStpy)_2]^{2+}$  cations in  $[Fe(4'-PhStpy)_2]$ [PF<sub>6</sub>]<sub>2</sub>·2MeCN associate through face-to-face  $\pi$ -stacking of pyridine rings, and twisting of the PhS substituents enables the cations to embrace one another, capturing four MeCN solvate molecules within the {Fe(4'-PhStpy)\_2}\_2-motif.

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Complexes containing  $\{M(tpy)_2\}^{n+}$  cores and featuring thiolterminated alkyl tethers are of interest in molecular electronics, the soft sulfur donor facilitating anchoring of the complexes on to, for example, gold or platinum surfaces [1-4]. In contrast, the coordination chemistry of 4'-RS-2,2':6',2"-terpyridine (4'-RStpy) ligands containing thiol or thioether substituents with the sulfur atom directly bonded to the tpy domain is still rather poorly explored. The synthetic strategy of Potts allows access to thioether derivatives (e.g., 4'-MeStpy, 4'-EtStpy, 4'-<sup>n</sup>PrStpy) [5,6], the latter being easily oxidized to sulfones [7]. For the 4'-thiol derivative 4'-HStpy, the thione tautomer is favored both in solution and in the solid state, and deprotonation of the complex  $[Fe(4'-HStpv)]^{2+}$  (isolated as its hexafluoridophosphate salt) results in neutral [Fe(Stpy)<sub>2</sub>] [8]. Oxidative coupling of 4'-HStpy provides a facile route to disulfide bridged tpySStpy ligands [9], and we have also described analogous interconversions involving 2,2':6',2"-terpyridine-6(1H)-thione [10]. Although 4'-RStpy (R = alkyl) ligands and their complexes are documented, 4'-PhStpy (Scheme 1) has not been previously reported. There are, rather surprisingly, few structurally characterized complexes of the type  $[M(4'-ArXtpy)_2]^{n+}$  in which Ar is a phenyl ring or part of a more extended aromatic system: Ar = Ph, X = NH, M = Fe; Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>, X = NH, M = Fe or Ru [11], Ar =Ph, X = P(O)Ph, M = Ru [12].

Reaction of 4'-chloro-2,2':6',2"-terpyridine with thiophenol at 170 °C yielded 4'-PhStpy, after workup, in 82% yield [13]. The  $^{1}$ H

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and <sup>13</sup>C NMR spectra [13] were consistent with the structure shown in Scheme 1 and were assigned using HMQC and HMBC methods. The structure of the compound (Fig. 1) was confirmed by single crystal X-ray diffraction [14]. The tpy domain adopts the expected *trans*, trans-configuration and is planar; angles between the least squares planes of rings with atoms N1/N2 and N2/3 are 2.2(2) and 6.1(3)°. The plane containing the phenyl substituent is twisted 64.3(3)° out of the plane of the central pyridine ring. The similarity of the two S-C bond distances (see Fig. 1 caption) and the value of  $104.0(3)^{\circ}$  for the C8–S1–C16 bond angle are consistent with an  $sp^{3}$ hybridized S atom and lack of any  $\pi$ -contribution to the C–S bond adjacent to the arene ring. This contrasts with the typical observation in 4'-ROtpy derivatives in which bond parameters in the solid state support  $\pi$ -contribution to the C<sub>arene</sub>-O bond [15], consistent with  $2p-3p \pi$ -orbital overlap being less effective than a  $2p-2p \pi$ interaction. Centrosymmetric pairs of molecules associate through non-classical CH ... N hydrogen bonds (C15H151 ... N3<sup>i</sup> = 2.67, C15 ...  $N3^{i} = 3.479(10)$  Å, C15–H151 ...  $N3^{i} = 145^{\circ}$ , symmetry code i = 3 - x, 1-y, -z and engage in face-to-face  $\pi$ -stacked interactions, leading to an assembly of separated tpy and SPh domains (Fig. 2).

Reaction of two equivalents of 4'-PhStpy with FeCl<sub>2</sub>·4H<sub>2</sub>O in MeOH followed by anion exchange (by addition of aqueous NH<sub>4</sub>PF<sub>6</sub>) leads to the formation of purple [Fe(4'-PhStpy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> [17]. The electrospray mass spectrum of the product exhibited peaks at m/z 882.8 and 369.4 (base peak) assigned to  $[M-PF_6]^+$  and  $[M-2PF_6]^{2+}$ , respectively. The isotope patterns were consistent with those calculated for these ions. The <sup>1</sup>H NMR spectrum of a CD<sub>3</sub>CN solution of the complex demonstrated the presence of one ligand environment, consistent with the formation of the homoleptic complex. Although solubility differences did not permit the NMR spectra to be recorded in a common

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Scheme 1. Structure of ligand 4'-PhStpy, and labeling scheme for NMR spectroscopic assignments.

solvent, a comparison of the <sup>1</sup>H NMR spectra of the free ligand and  $[Fe(4'-PhStpy)_2][PF_6]_2$  revealed a significant shift to lower frequency for the signal for protons H<sup>A6</sup> ( $\delta$  8.58 to 7.12 ppm). This is diagnostic of the formation of an {M(tpy)\_2} domain, with the H<sup>A6</sup> protons on one ligand lying over the ring current of the second tpy. The formation of the complex was confirmed by single crystal X-ray diffraction [18].

Fig. 3 shows the structure of the  $[Fe(4'-PhStpy)_2]^{2+}$  cation in  $[Fe(4'-PhStpy)_2][PF_6]_2 \cdot 2MeCN$ . The  $Fe^{2+}$  ion is in an octahedral environment and bond lengths and angles (see figure caption) are unexceptional. As in the free ligand, the bond angle at the sulfur atoms and the C–S bond distances indicate that there is no  $\pi$ -contribution to the Carene-S bonds. The phenyl rings attached to S1 and S2 are twisted at 66.39(13) and 76.48(12)°, respectively, with respect to the pyridine ring to which each SPh unit is attached. Centrosymmetric pairs of cations engage in a face-to-face  $\pi$ -stacking of pyridine rings containing atoms N3 and N3<sup>i</sup> (symmetry code i = 2 - x, -y, 1 - z). The separation of the planes of the rings is 3.58 Å and the centroid ... centroid distance is 3.82 Å making this an efficient interaction [19]. This interaction is supplemented by edge-to-face contacts (C13H131...centroid of ring containing  $N4^i = 2.54$  Å). More extensive  $\pi$ -interactions as commonly occur in the solid state structures of complexes containing  $\{M(tpy)_2\}$  units [20-24] are not operative. Instead, the pendant SPh groups of each enantiomer embrace one another (Fig. 4a) although there are no edge-to-face contacts between phenyl rings. Each cavity revealed in Fig. 4a hosts two MeCN molecules with short N...H<sub>pyridine</sub> contacts (C12H121 ...  $N9^{ii} = 2.46$  Å, C15H151...N10<sup>iii</sup> = 2.49 Å, symmetry codes: ii = -1 + 1x, y; iii = 3-x, -y, 1-z). The structural motifs shown in Fig. 4a assemble into chains through S ... H hydrogen bonds (C4H41 ...  $S1^{iv} = 2.85, C4 \dots S1^{iv} = 3.671(3)$ Å, C4H41...S1<sup>iv</sup> = 139°, symmetry code iv = 1 - x, 1 - y, 1 - z) as depicted in Fig. 4b.



**Fig. 1.** ORTEP [16] representation of the structure of 4'-PhStpy with ellipsoids (non H atoms) drawn at 30% probability. Selected bond parameters: C1 - N1 = 1.318(7), C5 - N1 = 1.330(7), C6 - N2 = 1.338(6), C10 - N2 = 1.326(6), C11 - N3 = 1.328(7), C15 - N3 = 1.318(7), C8 - S1 = 1.764(5), C16 - S1 = 1.759(6)Å; C5 - N1 - C1 = 117.5(5), C6 - N2 - C10 = 117.5(4), C11 - N3 - C15 = 118.0(5),  $C8 - S1 - C16 = 104.0(3)^{\circ}$ .



Fig. 2. Packing of molecules of 4'-PhStpy showing  $\pi$ -stacked tpy domains interleaved by domains of SPh substituents.



**Fig. 3.** ORTEP [16] representation of the structure of the  $[Fe(4'-PhStpy)_2]^{2+}$  cation in  $[Fe(4'-PhStpy)_2][PF_6]_2 \cdot 2MeCN$  (ellipsoids at 30% probability level). Selected bond parameters: Fe1-N1 = 1.9614(18), Fe1-N2 = 1.8741(18), Fe1-N3 = 1.9653(19), Fe1-N4 = 1.977(2), Fe1-N5 = 1.8805(18), Fe1-N6 = 1.9724(19), S1-C8 = 1.762(2), S1-C31 = 1.765(3), S2-C23 = 1.763(2), S2-C37 = 1.772(2)Å; N1-Fe1-N2 = 81.05(8), N2-Fe1-N3 = 81.50(8), N4-Fe1-N5 = 81.13(8), N5-Fe1-N6 = 81.15(8), C8-S1-C31 = 104.50(11), C23-S2-C37 = 102.18(11)°.



**Fig. 4.** (a) The embrace of  $[Fe(4'-PhStpy)_2]^{2+}$  enantiomers. (b) Association of pairs of cations through S ... H interactions.

In conclusion, we have prepared and characterized 4'-PhStpy which, despite its simplicity, is a new 2,2':6',2"-terpyridine derivative. The principal packing motif in  $[Fe(4'-PhStpy)_2][PF_6]_2 \cdot 2MeCN$  is a  $\{Fe(4'-PhStpy)_2\}_2$ -unit in which centrosymmetric pairs of  $[Fe(4'-PhStpy)_2]^2^+$  cations embrace one another. The motif is stabilized by a face-to-face  $\pi$ -stacking interaction, and captures two MeCN molecules in each of its two cavities.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.inoche.2012.03.003.

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- [13] 4'-Chloro-2,2':6',2"-terpyridine (150 mg, 0.56 mmol) and C<sub>6</sub>H<sub>5</sub>SH (130 mg, 1.18 mmol) were heated to 170 °C under N<sub>2</sub> for 4 h. Addition of Et<sub>2</sub>O gave a precipitate which was collected by filtration. The product was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> followed by CH<sub>2</sub>Cl<sub>2</sub>/MeOH 1:1) and then recrystallized by diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1) solution of the compound. 4'-PhStpy was isolated as a white crystalline solid (156 mg, 0.46 mmol, 82%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD)  $\delta$ /pm: 8.58 (d, J = 4.8 Hz, 2H, H<sup>A6</sup>), 8.53 (d, J = 7.9 Hz, 2H, H<sup>A3</sup>), 8.07 (s, 2H, H<sup>B3</sup>), 7.94 (td, J = 7.7, 1.8 Hz, 2H, H<sup>A4</sup>), 7.66 (m, 2H, H<sup>C2</sup>/C<sup>3</sup>), 7.53 (m, 3H, H<sup>C4+C2/C3</sup>), 7.42 (m, 2H, H<sup>A5</sup>). <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>OD)  $\delta$ /pm: 157.1 (C<sup>A2/B2</sup>), 157.0 (C<sup>A2/B2</sup>), 154.2 (C<sup>B4</sup>), 150.4 (C<sup>A6</sup>), 138.9 (C<sup>A4</sup>), 136.5 (C<sup>C2/C3</sup>), 131.5 (C<sup>C2/C3</sup>), 131.3 (C<sup>C4</sup>), 131.1 (C<sup>C1</sup>), 125.8 (C<sup>A5</sup>), 123.1 (C<sup>A3</sup>), 119.2 (C<sup>B3</sup>). IR (solid,  $\nu/cm^{-1}$ ) 2920 vs, 2851 s, 1728 w, 1573 s, 1556 vs, 1543 vs, 1465 vs, 1438 s, 1391 vs, 1326 m, 1265 m, 1143 m, 1068 m, 1037 m, 1024 m, 960 m, 874 m, 812 m, 787 vs, 741 vs, 727 vs.

- [14] 4'-PhStpy:  $C_{21}H_{15}N_3S$ , M = 341.44, colourless plate, monoclinic, space group  $P_{2_1/c}$ , a = 4.437(9), b = 37.81(4), c = 9.902(6)Å,  $\beta = 96.273(10)^\circ$ , U = 1651(4)Å<sup>3</sup>, Z = 4,  $D_c = 1.374$  mg m<sup>-3</sup>,  $\mu$ (Mo-K<sub>cc</sub>) = 0.204 mm<sup>-1</sup>, T = 173 K. Total 16471 reflections, 2997 unique,  $R_{int} = 0.1984$ . Refinement against *F* of 226 parameters using 2173 reflections with I > 20 (*I*) converged at final R1 = 0.0964 (*R1* all data = 0.1642), wR2 = 0.0822 (wR2 all data = 0.1542), gof = 0.9964.
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- $\begin{array}{l} \label{eq:16} \mbox{ [17] [Fe}(4'-PhStpy)_2] [PFe]_2: \ ^{1}H \ NMR (2510 \ MHz, CD_3 CN) \ \delta/ppm: 8.48 \ (s, 2H, H^{B3}), 8.20 \ (d, J = 7.9 \ Hz, 2H, H^{A3}), 7.94 \ (m, 2H, H^{C2/C3}), 7.80 \ (td, J = 7.8, 1.5 \ Hz, 2H, H^{A4}), 7.72 \ (m, 3H, H^{C4} + C^{2/C3}), 7.12 \ (d, J = 4.8 \ Hz, 2H, H^{A6}), 7.05 \ (m, 2H, H^{A5}). \ IR \ (solid, \nu/cm^{-1}) \ 3093 \ w, 1597 \ m, 1533 \ w, 1467 \ m, 1423 \ s, 1396 \ s, 1285 \ w, 1246 \ w, 1121 \ w, 1109 \ w, 1085 \ w, 825 \ w, 783 \ vs, 729 \ vs. \ ESI \ MS \ 882.8 \ [M-PF_6]^+ \ (calc. 883.1), 369.4 \ [M-2PF_6]^- \ (calc. 369.0). \ Found: \ C, 49.34; \ H, 2.99; \ N, 8.00; \ calculated \ for \ C_{42}H_{30}F_{12}FeN_6P_2S_2 \ C, 49.04; \ H, 2.94; \ N, 8.17\%. \end{array}$
- [18] [Fe(4'-PhStpy)\_][PF6]\_2·2MeCN: Ca6H<sub>36</sub>F<sub>12</sub>FeN<sub>8</sub>P<sub>2</sub>S<sub>2</sub>, *M*=1110.75, purple plate, triclinic, space group *P*-1, *a*=9.2931(6), *b*=15.9261(13), *c*=17.0422(6)Å,  $\alpha$ =75.124(4),  $\beta$ =80.979(5),  $\gamma$ =75.723(5)°, *U*=2350.7(3)Å<sup>3</sup>, *Z*=2, *D*\_{c}=1.569 mg m<sup>-3</sup>,  $\mu$ (Mo-K<sub> $\alpha$ </sub>)=0.570 mm<sup>-1</sup>, *T*=173 K. Total 89719 reflections, 11365 unique, *R*<sub>int</sub>=0.095. Refinement against *F* of 643 parameters using 7286 reflections with *I*>2 $\sigma$  (*I*) converged at final *R*1=0.0449 (*R*1 all data=0.0743), w*R*2=0.0414 (*wR*2 all data=0.0542), gof=1.1336.
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