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# An iron(II) spin crossover grafted cyclotriphosphazene

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#### ABSTRACT

The synthesis of the new cyclotriphosphazene (CTP) ligand substituted with a pendant 2,6-bis(benzimidazole-2-yl)pyridine (bbp), namely (pentaphenoxy)[4-{2,6-bis(benzimidazole-2-yl)pyridine-4-yl}phenoxy]cyclotriphosphazene **L** is reported. The single crystal structure of **L** shows that the bbp group is attached to the CTP via the oxygen. **L** reacts with FeX<sub>2</sub> (X =  $ClO_4^-$  or BF<sub>4</sub><sup>-</sup>) salts forming the [FeL<sub>2</sub>]X<sub>2</sub> complexes **1** and **2** respectively. For [FeL<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**2**), the single crystal structure shows an 'N<sub>6</sub>' coordination sphere around the iron atom. UV–Vis, resonance Raman and Mössbauer spectroscopies and magnetic susceptibility measurements, aided by density functional theory (DFT) calculations, determine the complexes are low spin below 300 K but display spin crossover (SCO) behavior above this temperature, hence showing that the addition of a phosphazene to a SCO moiety does not prevent SCO.

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## 1. Introduction

For many years, spin crossover (SCO) materials have been suggested as having potential for use in quantum computers and massive data storage systems for example [1,2]. However, because these materials are often crystalline, they are difficult and expensive to deposit and process. Previously we attempted to improve the processing properties by attaching pendant 2,2':6',2"-terpyridine (terpy) substituents to both cyclotri- and polyphosphazene (CTP and PP) (Scheme 1) and forming the subsequent iron(II) complexes [3]. The repeating nitrogen-phosphorus backbone provided an electronically mute scaffold for the metal–ligand centers; however, it was determined that only the start of SCO was observed at very high temperatures, preventing most practical applications [3].

The present study aims to improve on the terpy-based design by using a 2,6-bis(1*H*-benzimidazol-2-yl)pyridine (bbp) moiety attached to a CTP. The physical properties of the resultant iron(II) complexes were investigated using a variety of spectroscopic techniques, such as electronic absorbance, solid state resonance Raman and Mössbauer spectroscopy as well as magnetic susceptibility. DFT calculations were employed to obtain insight into the behavior of the compounds. Bbp was chosen, as iron(II)-bis-bbp ([Fe(bbp)<sub>2</sub>]<sup>2+</sup>) complexes are well known for their SCO behavior [4–8], thus should provide an improvement over terpy-based phosphazene complexes previously reported [3]. This is the first time phosphazene systems containing these imidazolyl-pyridyl species have been reported and it was of interest to determine if and how the substitution of the phosphazene alters their SCO behavior.

# 2. Experimental

Analytical grades of solvents were used. 2,6-bis(1*H*-benzimidazol-2-yl)pyridine-4(1*H*)-one (HObbp) [9] and 1,2,2,3,3-pentakis(phenoxy)-1-chlorocyclotriphosphazene, N<sub>3</sub>P<sub>3</sub>(OPh)<sub>5</sub>Cl, [10] were synthesized by literature methods. K<sub>2</sub>CO<sub>3</sub>, Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O were sourced from Aldrich–Sigma. To avoid iron(II) oxidation, all manipulations were carried out under an argon atmosphere, using standard Schlenk techniques.

*Caution!* Perchlorate salts with organic ligands are potentially explosive and should be handled with the necessary precautions.

#### 2.1. Synthesis of the compounds

2.1.1.  $[N_3P_3(OPh)_5(Obbp)]$  (L)

 $N_3P_3(OPh)_5Cl$  (195 mg, 0.31 mmol) was added to a solution containing HObbp (100 mg, 0.31 mmol) and K<sub>2</sub>CO<sub>3</sub> (45 mg, 0.33 mmol) in acetone (50 mL). After stirring at reflux for five days the solvent was removed under reduced pressure, leaving a pink solid that was washed with CHCl<sub>3</sub>/water and dried over MgSO<sub>4</sub>. A minimal amount of hexane was added to the solution to form a white precipitate. The precipitate was filtered and dried under vacuum for elemental analysis. Diffractable crystals were grown via a slow evaporation of an acetone/water solution. Yield: 140 mg (51%).



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**Scheme 1.** Generic polyphosphazene (PP) and cyclotriphosphazene (CTP) structures.

ESMS: m/z 927  $[N_3P_3(OPh)_5(Obbp)H]^+$ , 965  $[N_3P_3(OPh)_5(Obbp)K]^{+,31}P\{^{1}H\}$  NMR (CDCl<sub>3</sub>):  $\delta$  9.6 ppm (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.02 ppm (s, 2H), 7.40 (s, 2H), 7.05–7.00 (m, 10H), 6.95 (d (J = 8 Hz), 10H), 6.81 (t (8), 8H), 6.77 (d (8), 5H). *Anal.* Calc. for C<sub>49</sub> H<sub>37</sub>N<sub>8</sub>O<sub>6</sub>P<sub>3</sub>·<sup>2</sup>/<sub>3</sub>CHCl<sub>3</sub>: C, 59.28; H, 3.77; N, 11.13. Found: C, 59.18; H, 3.76; N, 11.06%.

#### 2.1.2. $[FeL_2](ClO_4)_2(1)$

To a stirred solution of **L** (100 mg, 0.11 mmol) in MeOH:CHCl<sub>3</sub> (1:1, 8 mL). Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (4.0 mg, 0.066 mmol) was added, immediately turning the solution purple. Stirring was continued for 30 min before the solvent was removed under reduced pressure. The solid was dissolved in CHCl<sub>3</sub> and filtered through Celite. The filtrate was dried under reduced pressure, leaving a purple solid. Weakly diffractable crystals were grown by dissolving the solid in acetone and diffusing in tert-butyl-methyl ether. Yield: 72 mg (62%). ESMS: m/z 955 [Fe(L)<sub>2</sub>]<sup>2+</sup>. <sup>31</sup>P{<sup>1</sup>H}MR (CD<sub>3</sub>CN):  $\delta$  11.28 ppm (d (93 Hz), 4P), -44.09 (t (93), 2P). <sup>1</sup>HNMR (CD<sub>3</sub>CN):  $\delta$  14.48 ppm (4H), 9.00 (4H), 8.06 (4H), 7.85 (20H), 7.67 (10H), 7.57 (20H), 6.73 (4H), 6.32 (4H), 6.17 (4H). Anal. Calc. C<sub>98</sub>H<sub>74</sub>Cl<sub>2</sub> FeN<sub>16</sub>O<sub>20</sub>P<sub>6</sub>·C<sub>5</sub>H<sub>12</sub>O·2H<sub>2</sub>O: C, 55.41, H, 4.06; N, 10.04. Found: C, 55.26; H, 4.01; N, 10.01%.

### 2.1.3. [FeL2](BF4)2 (2)

The same procedure as for **1** was used, except  $Fe(BF_4)_2 \cdot 6H_2O$  was used in place of  $Fe(ClO_4)_2 \cdot 6H_2O$ . Diffractable crystals were grown by dissolving the solid in acetone and diffusing in tertbutyl-methyl ether. Yield: 70 mg (63%). ESMS: m/z 955 [ $Fe(L)_2$ ]<sup>2+</sup>. <sup>31</sup>P{<sup>1</sup>H}NMR (CD<sub>3</sub>CN):  $\delta$  11.6 ppm (d (93 Hz), 4P), -41.9 (t (93), 2P). <sup>1</sup>HNMR (CD<sub>3</sub>CN):  $\delta$  14.60 ppm (4H), 8.94 (4H), 8.04 (4H), 7.84 (20H), 7.61 (10H), 7.57 (20H), 6.84 (4H), 6.64 (4H), 6.11 (4H). Anal. Calc.  $C_{98}H_{74}Cl_2FeN_{16}O_{20}P_6 \cdot ^3/_4C_5H_{12}O \cdot H_2O$ : C, 56.39; H, 3.95; N, 10.34. Found: C, 56.34; H, 4.02: N, 10.39%.

#### 2.2. Crystallographic studies

The X-ray data were collected at low temperature with a Rigaku-Spider X-ray diffractometer, comprising a Rigaku MM007 microfocus copper rotating-anode generator, high-flux Osmic monochromating and focusing multilayer mirror optics (Cu K radiation,  $\lambda = 1.5418$  Å), and a curved image-plate detector. *CrystalClear* was utilized for data collection and *FSProcess* in *PROCESS-AUTO* was used for cell refinement and data reduction. Crystal refinement data are given in Table 1. The structures were solved by direct methods and refined using both the SHELXTL [11] and OLEX2 [12] programs. Hydrogen atoms were calculated at ideal positions.

For the solution of  $2 \cdot C_3 H_6 O \cdot C_5 H_{12}O$ , the electron density (15 e<sup>-</sup> per cell in a void volume of 118.5 Å<sup>3</sup>) of the occupationally and positionally disordered acetone molecule was removed by using PLATON/SQUEEZE [13].

### 2.3. Physical measurements

Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago, New Zealand and assigned using

Table 1Crystal and Refinement Data for  $L \cdot 3H_2 O \cdot C_3 H_6 O$  and  $2 \cdot C_3 H_6 O \cdot C_5 H_{12} O$ .

Compound	L·3H <sub>2</sub> O·C <sub>3</sub> H <sub>6</sub> O	$2 \cdot C_3 H_6 O \cdot C_5 H_{12} O$
Molecular formula M (g mol <sup>-1</sup> ) T (K)	C <sub>52</sub> H <sub>49</sub> N <sub>8</sub> O <sub>10</sub> P <sub>3</sub> 1038.91 163(2)	C <sub>106</sub> H <sub>92</sub> B <sub>2</sub> F <sub>8</sub> FeN <sub>16</sub> O <sub>14</sub> P <sub>6</sub> 2229.26 123(2)
Crystal system	triclinic	triclinic
Space group	ΡĪ	$P\bar{1}$
a (Å)	11.8419 (4)	12.880(3)
b (Å)	14.0379 (4)	17.690(4)
<i>c</i> (Å)	15.3918 (11)	24.070(5)
α (°)	91.665 (7)	85.16(3)
β (°)	90.322 (6)	83.21(3)
γ (°)	96.231 (2)	75.32(3)
$V(Å^3)$	2542.4 (2)	5259.6(21)
Ζ	2	2
$\mu$ (Cu K $\alpha$ ) (mm <sup>-1</sup> )	1.634	2.736
$ ho_{ m calc} ({ m g}{ m cm}^{-3})$	1.357	1.407
$2\theta_{\max}$ (°)	117.88	102.26
Number of unique reflections	7193	11111
Data/restraints/parameters	7193/60/685	11111/2766/1494
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0756$	$R_1 = 0.0916$
	$wR_2 = 0.1775$	$wR_2 = 0.2155$
R indices (all data)	$R_1 = 0.1347$	$R_1 = 0.1137$
	$wR_2 = 0.2407$	$wR_2 = 0.2296$
Goodness-of-fit (GOF) on $F^2$	1.074	0.967

CHN [14]. <sup>31</sup>P{<sup>1</sup>H} NMR measurements were carried out on a Bruker Avance 400 spectrometer and <sup>1</sup>H NMR on a Bruker Avance 500 spectrometer. Electrospray mass spectra were obtained from acetonitrile solutions on a Micromass ZMD spectrometer run in the positive ion mode. Listed peaks correspond to the most abundant isotopomer; assignments were made by a comparison of observed and simulated spectra. All ground state vibrational measurements were made using KBr disks on a Nicolet 5700 FT-IR spectrometer. Continuous wave excitation was used for all Raman measurements. UV-Vis absorbance spectra were recorded using an Oceans Optics USB2000 + UV-Vis spectrophotometer on solutions prepared by dissolving the solid complexes in acetonitrile. Cvclic voltammetry was obtained using a glassy carbon working electrode. Pt counter electrode and Ag/AgCl reference electrode;  $v = 0.1 \text{ V s}^{-1}$  recorded in acetonitrile, 0.1 M TBAClO<sub>4</sub> at  $10^{-3}$  for the complexes **1**; 0.1 M TBABF<sub>4</sub> at  $10^{-3}$  for **2**.

Resonance Raman measurements were carried out based on a modified version of a system described previously [15-17]. Spectra were acquired of solid-state samples at 79, 298 and 362 K with a number of excitation wavelengths. Temperature control was achieved by utilizing a variable temperature cell (Specac, Woodstock, GA, USA) and a high stability temperature controller (Specac, Woodstock, GA, USA). Vacuum-purging of the cell was used to minimize condensation and frosting of the quartz window of the variable temperature cell. For excitation at 350.7 and 568.2 nm, a continuous-wave Innova I-302 krypton-ion laser (Coherent, Inc.) was used. For excitation at 457.9 and 514.5 nm an Innova Sabre DBW argon-ion laser (Coherent, Inc.) was used. The beam was passed through either a Pellin-Broca prism (for 350.7, 457.9 and 514.5 nm) or a holographic laser band pass filter (Kaiser Optical Systems, Inc.) and subsequently two irises in order to remove unwanted laser-lines. The beam-power was adjusted between 20 and 40 mW at the sample, depending on the wavelength used. The sample and collection lens were arranged in a 180 backscattering geometry where the collection lens also served to focus the excitation beam on the sample. The Raman photons were focused on the entrance slit of an Acton Research SpectraPro500i spectrograph (Princeton Instruments, Inc.) with a 1200 grooves mm<sup>-1</sup> grating. The slit width was set to 50  $\mu$ m, giving a resolution of ca. 2 cm<sup>-1</sup> Radiation from Raleigh and Mie-scattering was attenuated using a notch filter (Kaiser Optical Systems, Inc.) for 568.2 nm and Razor Edge filters (Semrock, Inc.) for other wavelengths. The dispersed photons were detected using a Princeton Instruments liquid nitrogen cooled 1152-EUV charge-coupled detector controlled by a Princeton Instruments ST-130 controller. WinSpec/32 software (Roper Scientific, Inc.) was used to control the CCD, and spectra were analyzed using GRAMS/32 (Galactic Industries Corp.) software. Wavelength calibration was achieved using a reference sample made from 1:1 toluene:acetonitrile and general alignment was done using a solid sample of carbamazepine.

<sup>57</sup>Fe Mössbauer spectra were recorded using approximately 30 mg of sample placed in a nylon sample holder (12.8 mm diameter, 1.6 mm thickness) with Kapton windows. The spectra were measured on a Mössbauer instrument from SEE Co. (Science Engineering & Education Co., MN) equipped with a closed cycle refrigerator system from Janis Research Co. and SHI (Sumitomo Heavy Industries Ltd.). 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 conducted using the WMOSS program (SEE Co., formerly WEB Research Co., Edina, MN).

Magnetic susceptibilities were determined using a Quantum Design Inc. Squid MPMS5 magnetometer with the  $\sim$ 25 mg samples held in a calibrated gel capsule that was placed in the center of a drinking straw that was fixed to the end of the sample rod. A DC field of 1 T was used. The instrument was calibrated against a Pd

pellet of accurately known susceptibility provided by Quantum Design Inc. and checked against the temperature-dependent behavior of CuSO<sub>4</sub>·5H<sub>2</sub>O.

## 2.4. Computational

Density functional theory (DFT) calculations were carried out using the Gaussian09 package (Gaussian, Inc) [18]. Frequency and time-dependent (TD) calculations were performed on optimized ground-state structures, all results were displayed using GaussView [19]. All calculations used the 6-31G(d) basis set employing two different levels, OLYP and B3LYP. The vibrational spectra generated by both levels were compared to the measured vibrational data determining OLYP to be the most accurate level. An unambiguous assignment of vibrational modes from visual comparison of spectra was possible for most peaks. TD-DFT calculations were carried out in an acetonitrile solvent field using the SCRF-PCM method which creates the solvent cavity via a set of overlapping spheres. Geometry optimizations were not carried out in a solvent field, as these are difficult to achieve for molecules this size; however, correlation is found to be better than for calculations where solvent contributions have been completely neglected.

The two different levels for computational models (B3LYP and OLYP) with a 6-31G(d) basis were compared to vibrational data collected to determine which was the most accurate in addition



 $X = CIO_4^{-}(1)$  $X = BF_4^{-}(2)$ 



Fig. 1. Crystal structure of L. Hydrogen atoms and solvate species removed for clarity.



Fig. 2. Crystal structure of 2. Hydrogen atoms, disordered atoms, solvate species and anions removed for clarity.

to validating the models. Higher level basis sets were not explored due to the size of the molecule making such calculations unfeasible. The B3LYP frequencies were scaled by 0.9613 [20] and OLYP by 0.9782 [21]. The assignments of the spectra were made using

each level and the MAD values determined for all of the assigned peaks (Supplementary data Table S2.1). These values indicated that there was little difference between the levels, but a comparison between the measured and calculated bond lengths indicated that

Table 2Electrochemical data for compounds 1 and 2.

Complex	$E_{\nu_{20x}}$ (V) ( $\Delta E_{p}$ , mV)	$E_{1/2}$ red (V) ( $\Delta E_{p}$ , mV)	$E_{1/2}$ red (V) ( $\Delta E_{p}$ , mV)
1	0.575 (135)	-0.930 (317)	–1.474 (irr)
2	0.550 (108)	-0.912 (190)	–1.556 (irr)

the OLYP models were an order of magnitude more accurate than the B3LYP models (Supplementary data Table S2.2).

## 3. Results and discussion

#### 3.1. Synthesis

The phosphazene ligand **L** was synthesized by reacting the potassium salt of HObpp with  $N_3P_3(OPh)_5Cl$  (Scheme 2) for 5 days. As with the 2,6-bis(2-pyridyl)-4(1*H*)-pyridone substituted phosphazene [3], HObpp is most stable in the enone tautomer; this consequently lowers the acidity of the phenol, reducing the reactivity.

In addition, to prevent the reactions with the imidazole proton, a carbonate base was used in place of a hydride. As a final factor, HObpp had limited solubility in THF, therefore it was necessary to use acetone, a solvent with a much lower boiling point.

The iron(II) complexes, **1** and **2**, were synthesized by reacting two equivalents of the **L** with one equivalent of the appropriate iron salt,  $Fe(ClO_4)_2$ · $6H_2O$  or  $Fe(BF_4)_2$ · $6H_2O$ , dissolved in  $CHCl_3/CH_3OH$  (Scheme 2). The reactions occurred rapidly at room temperature to produce purple solutions from which the air stable, solid products were isolated. NMR coupling data were unavailable for the iron complexes due to the complexes being slightly paramagnetic in solution even below room temperature.

# 3.2. Molecular structures

The crystal structure of L (Fig. 1) shows the Obbp group attached to a phosphorus atom via the oxygen atom consistent with the spectroscopic data collected. In addition, no interactions are observed between any of the substituent groups and the phosphazene ring; this is an indication that if the polymer were synthesized it



Fig. 3. Left: the visible spectrum of 1 from 253–343 K. Right:  $\varepsilon_{MCLT}$  vs. temperature for (1) (black squares) and 2 (red circles).



Fig. 4. Molecular orbitals associated with the 548 nm transition (phenoxy groups and phosphazene ring removed for clarity).



Fig. 5. rR collected for 2. Left:  $\lambda_{ex}$  568 nm. Right:  $\lambda_{ex}$  514 nm.

would not decay via substituent effects; see Supplementary data (Table S1.1) for bond lengths and angles. The iron(II) compound **2** shows an 'N<sub>6</sub>' coordination sphere, consistent with the spectroscopic data collected (Fig. 2). The iron–nitrogen bond lengths are Fe(1)–N(1A) 1.920 (6), Fe(1)–N(2A) 2.005(5), Fe(1)–N(3A) 2.002 (6), Fe(1)–N(1B) 1.903 (6), Fe(1)–N(2B) 1.995 (6) and Fe(1)–N(3B)2.003 (6) Å, consistent with a low spin(LS) iron(II) bbp complex [4]. The phosphazene rings of **2** also exhibit little change as a result of the metal coordination (see Supplementary data Table S2). The tetrafluoroborate anions only display weak bonding with the hydrogens of the cationic complex, filling in the cavities; therefore, it can be assumed that the perchlorate anion of the isomorphous but poorly diffracting **1** will reside in an analogous position.

#### 3.3. Electrochemistry

Cyclic voltammetry measurements determined that each of the complexes had one reversible oxidation potential associated with the iron center and two reductions associated with the ligand (see Table 2). The oxidation potentials of **1** and **2** differed by 25 mV providing further evidence that the anions were interacting with the complex. In addition, the oxidation potentials are cathodically shifted relative to unsubstituted complex,  $[Fe(bbp)_2]$ 



Fig. 6. Vibrational mode assigned to  $1556 \text{ cm}^{-1}$  for HS-[Fe(L)<sub>2</sub>]<sup>2+</sup>, red arrows indicate displacement vectors.

 $(ClO_4)_2(0.415 \text{ V})$  [22] by 160–133 mV respectively, indicative of the phosphazene being an electron-withdrawing group.

# 3.4. Electronic spectroscopy

The temperature dependent electronic spectra for **1** are shown in Fig. 3. Both **1** and **2** display identical MLCT bands, with  $\lambda_{max}$  at 560 and 561 nm respectively, typical of LS  $t_{2g}^{6}$  forms of  $[Fe(bbp)_{2}]^{2+}$ complexes [23]. There are red shifts of 8 and 9 nm, respectively, relative to the unsubstituted complex  $[Fe(bbp)_2](ClO_4)_2$  ( $\lambda_{max}$  552 nm in acetonitrile) [23], which can be explained by the slight electronwithdrawing effects of the phosphazene ether unit, as previously reported [3,17,24,25]. Beyond this, the first ten calculated transitions with nonzero oscillator strengths can be found in the Supplementary Data (Table S3.1). The lowest-energy peaks have been attributed to MLCT transitions. Fig. 4 shows some of the molecular orbitals of 1 and 2 involved in the transition with the largest oscillator strength (548 nm, see Supplementary data), which can be described as H-1 and H-2  $\rightarrow$  L, L+1, L+2 and L+3. As the transition involves a net electron shift from the iron to the bbp ligand, this is consistent with the assignment of MLCT with no observable orbital overlap with the phosphazene ring.

The extinction coefficient ( $\varepsilon$ ) of the MLCT band decreased as the temperature was increased as expected for SCO behavior. However, a plot of the  $\varepsilon_{MCLT}$  versus temperature revealed a significant difference in the behavior of **1** and **2** (see Fig. 3). Baitalik and coworkers demonstrated that ruthenium-bpp complexes could hydrogen bond with the anions via imidazole protons resulting in different physical properties based on the anion present [26] which possibly explains the difference. In addition, neither plot shows the two plateaux expected for a Boltzmann distribution of HS and LS species. This has previously been observed and explained by Linert et al. [23] and explained as arising from an equilibrium formed between the complex and a coordinating solvent (e.g. acetonitrile or benzonitrile).

$$[\text{FeL}_2]^{2+} \rightleftharpoons [\text{FeL}(\text{PhCN})_3]^{2+} + L \rightleftharpoons [\text{Fe}(\text{PhCN})_6]^{2+} + 2L$$

The combination of each of these processes means that the thermodynamic parameters of the SCO process could not be determined even if it was occurring.

## 3.5. Vibrational spectroscopy

FT-IR spectra are dominated by aromatic ring deformations and anion vibrations therefore solid-state resonance Raman (rR) was employed to specifically investigate the behavior of the iron-bbp



Fig. 7. Magnetic moment  $\mu_{\text{eff}}$  vs. temperature. Left: 1, Right: 2. Black squares (1st run), red triangles (2nd run), blue diamonds (3rd run).

center as a function of temperature. rR is well suited to this as it shows selective enhancement of modes within active chromophores, where the excitation wavelength ( $\lambda_{ex}$ ) determines which particular chromophore is being probed [17]. The spectra were collected at  $\lambda_{ex}$  568.2 and 514.5 nm (exciting the MLCT transition) (Fig. 5). Assignments of modes from the other excitation wavelengths  $\lambda_{ex}$  are included in the Supplementary Data (Table S4.1). Spectra were recorded at 80, 298 and 362 K to observe the presence of both the HS and LS species. By comparison to DFT models, the enhanced vibrational modes were found to primarily consist of the benzimidazole and pyridine ring distortions. Significant activity of the chelating nitrogen atoms was observed, which is consistent with the assignment of the electronic transitions as MLCT.

As the temperature was increased, changes in the rR spectra were observed; for example, additional peaks were observed at  $1556 \text{ cm}^{-1}$  (Fig. 5). Comparison to a high spin (HS) DFT model allowed a tentative assignment of the differences to the formation of the HS species (Fig. 6).

#### 3.6. Magnetic susceptibility

Shown in Fig. 7 are plots of the magnetic moments ( $\mu_{eff}$ ) versus temperature for 1 and 2. Each of the complexes displayed an increase in  $\mu_{eff}$  as the temperature was increased. Due to the danger of heating a perchlorate salt, 1 could not be heated beyond 300 K. As a result only the start of the spin transition curve was observed. The LS form gave moment values, below  ${\sim}250$  K, of close to zero, as expected. However, for 2 the complex could be heated to 400 K (the limitation of the SQUID). The complex displayed a full SCO curve with a  $T_{\frac{1}{2}}$  at 336 K (Fig. 7, 1st run). In addition, after heating 2 beyond 350 K solvent was lost from the lattice, greatly altering the magnetic behavior of the complex, which does not completely return to the LS state upon cooling (Fig. 7, 2nd run). Successive heating resulted in a further loss of solvent, further altering the magnetic behavior (Fig. 7, 3rd run), trapping it in a spin state that has more HS character than has the parent. The precise make-up of the spin state(s) of the partially desolvated forms, below  $T_{1/2}$ , requires further detailed studies such as Mössbauer spectra and powder X-ray diffraction vs. temperature.

#### 3.7. Mössbauer spectroscopy

As a final means of investigating the coordination mode and spin state of the complexes, variable temperature Mössbauer spectroscopy was employed. Natural abundance iron provided an



Fig. 8. Mössbauer spectra of 1 and 2 recorded at 4.6 K.

Table 3<sup>57</sup>Fe Mössbauer data for complexes 1 and 2.

	<i>T</i> (K)	$\delta$ (mm s <sup>-1</sup> )	$\Delta E_{\rm Q} ({\rm mm}~{ m s}^{-1})$
1	4.6	0.35	0.47
	200	0.32	0.46
	294	0.29	0.47
2	4.6	0.34	0.45
	295	0.29	0.48
2	294 4.6 295	0.29 0.34 0.29	0.47 0.45 0.48

acceptable signal-to-noise ratio and therefore isotope enrichment was not employed. Spectra were recorded at 4.7, 200 and 293 K. Each of the complexes (**1** and **2**) displayed a quadrupole doublet with parameters ( $\delta$  and  $\Delta E_Q$ ) characteristic of LS [Fe(bbp)<sub>2</sub>]<sup>2+</sup> complexes (see Fig. 8 and Table 3) which is consistent with the crystal structure and magnetic data obtained. Neither complex displayed a significant change in its Mössbauer parameters as the temperature was increased (see Table 3); the small change in isomer shift is due to the second-order Doppler effect [27]. The slight asymmetry in the line widths is most likely a texture effect caused by preferred orientation of the crystallites in the sample [28]. The data are therefore consistent with the magnetic data, as all measurements were below the SCO temperature, due to the limitations of the Mössbauer instrument.

#### 4. Conclusions

A new CTP ligand L containing a bbp moiety was synthesized by reacting the potassium salt of HObbp with N<sub>3</sub>P<sub>3</sub>(OPh)<sub>5</sub>Cl. Iron(II) complexes were synthesized by the reaction of two equivalents of **L** with one equivalent of the appropriate iron(II) salts. Fe(ClO<sub>4</sub>)<sub>2-</sub>  $\cdot 6H_2O$  or Fe(BF<sub>4</sub>)<sub>2</sub> $\cdot 6H_2O$ , to afford **1** and **2**. The single crystal X-ray structure of **2** showed an ' $N_6$ ' coordination sphere typically formed for [Fe(bbp)<sub>2</sub>]<sup>2+</sup> complexes. The iron–nitrogen bond lengths corresponded to an LS complex. In addition, as both tetrafluoroborate and perchlorate anions are weakly coordinating tetrahedral anions, it is reasonable to assume that 1 has an isomorphous structure to 2. UV-Vis spectroscopy of the Fe(II) complexes displayed an MLCT band that is slightly red-shifted by about 8 nm with respect to the discrete  $[Fe(bbp)_2]^{2+}$  complex. Through the use of rR, aided by TD-DFT calculations, it was determined that the phosphazene did not contribute to this transition, rather it originated from the [Fe(bbp)<sub>2</sub>]<sup>2+</sup> core. In addition, the MLCT band extinction coefficient,  $\varepsilon$ , decreased as the sample was heated in solution, and although typical for SCO, analysis of this was complicated by a series of equilibria associated with solvent coordination. The combination of variable temperature solid-state rR, magnetic and Mössbauer spectroscopy confirmed the crystallographic data, that at low temperatures the complexes are LS but beyond 300 K they crossover to HS. This investigation proves that the addition of a phosphazene to a SCO moiety does not prevent SCO and provides a new route for the creation of workable SCO materials based on the polyphosphazene scaffold.

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# Appendix A. Supplementary data

CCDC 904683 and 904684 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.poly.2013.02.065.

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