

# How Does a Coordinated Radical Ligand Affect the Spin Crossover Properties in an Octahedral Iron(II) Complex?\*

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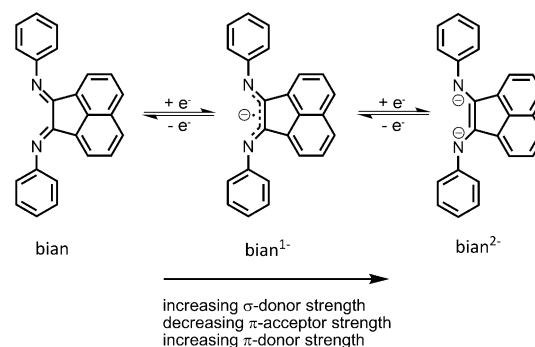
Dedicated to Professor Otto J. Scherer on the occasion of his 80th birthday

**Abstract:** The influence of a coordinated  $\pi$ -radical on the spin crossover properties of an octahedral iron(II) complex was investigated by preparing and isolating the iron(II) complex containing the tetradentate  $N,N'$ -dimethyl-2,11-diaza[3.3]-(2,6)pyridinophane and the radical anion of  $N,N'$ -diphenyl-acenaphthene-1,2-diimine as ligands. This spin crossover complex was obtained by a reduction of the corresponding low-spin iron(II) complex with the neutral diimine ligand, demonstrating that the reduction of the strong  $\pi$ -acceptor ligand is accompanied by a decrease in the ligand field strength. Characterization of the iron(II) radical complex by structural, magnetochemical, and spectroscopic methods revealed that spin crossover equilibrium occurs above 240 K between an  $S = 1/2$  ground state and an  $S = 3/2$  excited spin state. The possible origins of the fast spin interconversion observed for this complex are discussed.

The current growing interest in studying spin crossover (SCO) complexes is indebted to the potential application of such materials in molecular devices.<sup>[1]</sup> SCO processes are defined as entropy-driven redistributions of electrons among the d-orbitals of a metal ion as a consequence of altering the temperature or the pressure.<sup>[2]</sup> Furthermore, spin interconversions can be triggered by other external perturbations, such as light irradiation. Temperature-induced SCO in iron(II) complexes, for example at a spin-crossover transition temperature around 130 K, is observed where the enthalpy and the entropy difference between the excited high-spin state of a complex and the low-spin ground state ranges from 6–15 kJ mol<sup>-1</sup> and 40–65 J mol<sup>-1</sup> K<sup>-1</sup>, respectively.<sup>[2a]</sup> Therefore, to establish SCO properties in a specific metal complex,

the ligand field (one major aspect that determines the enthalpy difference) must be adjusted to an appropriate value by tuning the respective ligand field contribution of the ligand environment with respect to that of the metal ion.<sup>[3]</sup> One possible strategy to adjust the ligand field strength of a specific ligand focuses on exploiting the redox properties of the ligand. Herein, we present the results of such an investigation, leading, to the best of our knowledge, to the first iron(II) SCO complex that contains a directly to the metal ion coordinated radical ligand that exerts a marked influence on the properties of the spin crossover at the iron site. In addition, both oxidation states of this redox couple were isolated and characterized by various physical methods.

We have shown that octahedral iron(II) complexes containing the auxiliary tetradentate diazapyridinophane ligand L-N<sub>4</sub>Me<sub>2</sub> can display SCO properties with a multitude of bidentate or monodentate co-ligands.<sup>[4]</sup> Furthermore, acenaphthene-1,2-diimines (bian) are redox-active diimines,<sup>[5]</sup> which have been employed in the mono-reduced oxidation state in a variety of metal complexes.<sup>[6]</sup> Upon reduction of the neutral ligand to the single-reduced (bian<sup>1-</sup>) or the double-reduced oxidation state (bian<sup>2-</sup>), the  $\sigma$ - and the  $\pi$ -donor strengths of the ligand increase, while the  $\pi$ -acceptor strength is reduced (Scheme 1). Thus, without knowing which of these



**Scheme 1.** Dependence of the properties of the ligand bian on its oxidation state.

effects prevails, the influence of changing the redox-state of the coordinated bian on the spin-crossover capabilities of the iron(II) ion is uncertain.

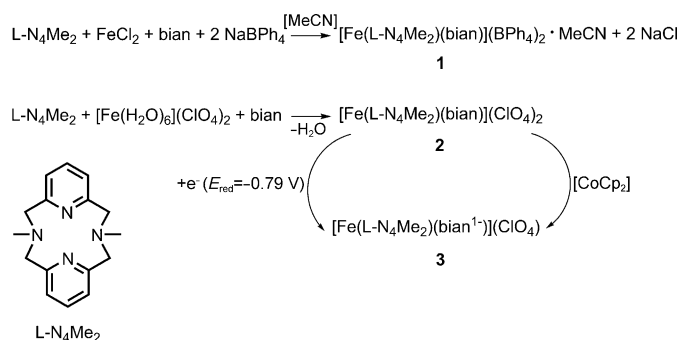
The starting point of this study is the synthesis of an iron(II) complex containing the auxiliary ligand L-N<sub>4</sub>Me<sub>2</sub> and the neutral ligand bian (Scheme 2), resulting in the isolation

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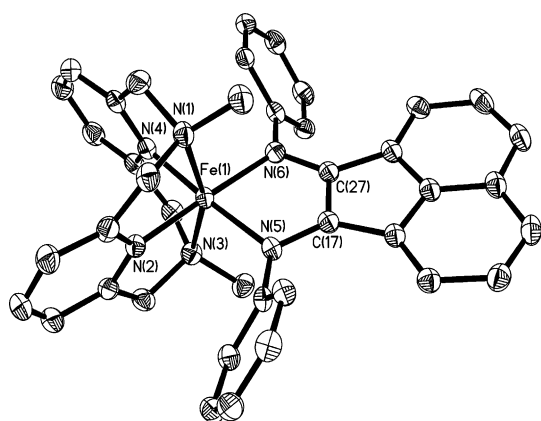
**Scheme 2.** Preparation of compounds **1–3**.

of the analytically pure compounds  $[\text{Fe}(\text{L-N}_4\text{Me}_2)(\text{bian})](\text{BPh}_4)_2 \cdot \text{MeCN}$  (**1**) and  $[\text{Fe}(\text{L-N}_4\text{Me}_2)(\text{bian})](\text{ClO}_4)_2$  (**2**).<sup>[7]</sup> The structure of **1** at 150 K was determined;<sup>[7]</sup> selected bond lengths are listed in Table 1. The overall structure of the complex cation resembles that depicted in Figure 1. As

**Table 1:** Selected bond lengths [Å] in **1** and **3**.

	<b>1</b> [150 K]	<b>3</b> [150 K]	<b>3</b> [293 K]	<b>3</b> [383 K]
Fe(1)–N(1)	2.077(2)	2.077(2)	2.113(3)	2.231(4)
Fe(1)–N(2)	1.911(2)	1.906(2)	1.940(3)	2.070(3)
Fe(1)–N(3)	2.088(2)	2.087(2)	2.125(3)	2.245(4)
Fe(1)–N(4)	1.915(2)	1.906(2)	1.943(3)	2.063(3)
Fe(1)–N(5)	1.962(2)	2.013(2)	2.023(3)	2.083(4)
Fe(1)–N(6)	1.962(2)	1.984(2)	1.995(3)	2.064(3)
C(17)–N(5)	1.306(3)	1.348(2)	1.356(4)	1.361(5)
C(27)–N(6)	1.313(3)	1.345(2)	1.337(4)	1.315(5)
C(17)–C(27)	1.461(3)	1.410(3)	1.418(5)	1.432(5)

usually observed in many octahedral metal complexes containing the ligand  $\text{L-N}_4\text{Me}_2$ , the coordinated tetraazamacrocycle is folded along the  $\text{N}_{\text{amine}}\text{--N}_{\text{amine}}$  axis, leaving two *cis*-oriented coordination sites to bian.<sup>[4,8,9]</sup> The averaged  $\text{Fe--N}_{\text{py}}$  and  $\text{Fe--N}_{\text{amine}}$  bond lengths of 1.913 and 2.082 Å, respectively,



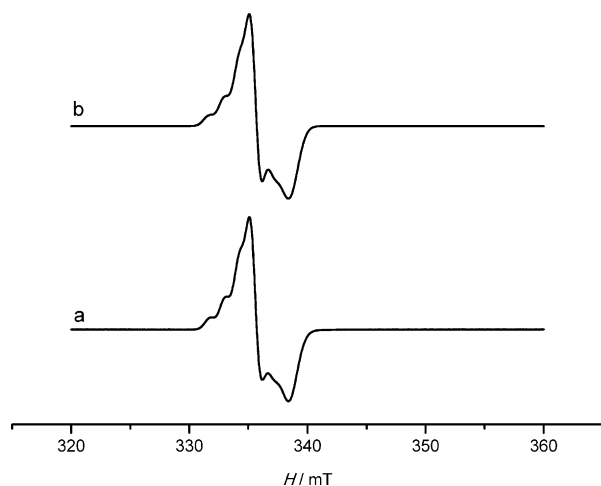
**Figure 1.** Perspective view of the complex cation in **3** (with thermal ellipsoids set at 50% probability) and the atom numbering scheme. Hydrogen atoms are omitted for the purpose of clarity. (The complex cation in **1** possesses an analogous overall structure; the same atom numbering was applied.)<sup>[18]</sup>

are characteristic for a low-spin state of the iron(II) ion.<sup>[4]</sup> The C–C and the C–N bond lengths within the diimine functional unit of the ligand bian, measuring 1.461 and 1.310 Å, respectively, are consistent with the oxidation state of the neutral ligand. Compared to the free ligand,<sup>[7]</sup> upon coordination these C–C and C–N bonds are shortened and lengthened, respectively, demonstrating the  $\pi$ -acceptor quality of the neutral ligand bian. The measurement of the magnetic moments of solid compound **2** between 2 and 380 K (Figure 4), the NMR spectra of compounds **1** and **2** in  $[\text{D}_3]\text{MeCN}$ ,<sup>[7]</sup> and the isomer shifts and the splittings of the quadrupole doublet in the Mössbauer spectra<sup>[7]</sup> of solid **2** between 70 and 383 K (70 K:  $\delta_{\text{IS}} = 0.29 \text{ mm s}^{-1}$  and  $\Delta E_{\text{Q}} = 1.37 \text{ mm s}^{-1}$ ) confirm the diamagnetic low-spin state of the iron(II) complex.<sup>[10]</sup> In addition, the NMR spectrum demonstrates that the complex is stable in solution.

The cyclic voltammogram of **2** in  $\text{MeCN}$ <sup>[7]</sup> reveals two reduction processes at  $E_{1/2} = -0.59$  and  $-1.10 \text{ V}$  vs. SCE, which are attributed to ligand-based reductions of coordinated bian to  $\text{bian}^{1-}$  and  $\text{bian}^{2-}$ . Compared to the free ligand, the redox reactions of the coordinated ligand are reversible on the cyclic voltammetric timescale. Apart from the reductions, the cyclic voltammogram of **2** shows a reversible oxidation at  $+1.10 \text{ V}$  vs. SCE corresponding to the oxidation of the metal ion to the trivalent oxidation state. Coulometric experiments show that one electron per molecule is transferred by reducing **2** at  $-0.79 \text{ V}$  and that the color of the solution changes from dark-green to dark-red. The recovery of 96 % of the original species upon immediate reoxidation at  $-0.39 \text{ V}$  indicates that the reduced species displays enough stability to warrant its isolation.

Quantitative electrolytic reduction of a solution of **2** in acetonitrile and subsequent isolation of the product renders analytically pure  $[\text{Fe}(\text{L-N}_4\text{Me}_2)(\text{bian}^{1-})](\text{ClO}_4)$  (**3**) in 50 % yield. The reduced complex can be more conveniently prepared from **2** by chemical reduction with one equivalent of cobaltocene in larger amounts and in slightly higher yields.<sup>[7]</sup> Suitable crystals were structurally investigated at various temperatures. A perspective view of the complex monocation in **3** is presented in Figure 1. Selected bond lengths obtained from crystal structure determinations at 150, 293, and 383 K are compared in Table 1. At 150 K, the averaged  $\text{Fe--N}_{\text{py}}$  and  $\text{Fe--N}_{\text{amine}}$  bond lengths of 1.906 and 2.081 Å, respectively, are almost identical to those found in the complex of **1**, indicating a low-spin state in the iron(II) ion in **3**. While the structural properties are almost unchanged within the iron(II) diazapyridinophane fragment, substantial changes occur on the bian side of the complex. Thus, the  $\text{Fe--N}_{\text{bian}}$  bonds increase in length by 0.036 Å on average. Furthermore, an appreciable deviation from the symmetric binding mode of the coordinated ligand is observed upon reduction of the complex, as detected by the noticeable difference in the length between the two  $\text{Fe--N}_{\text{bian}}$  bonds. Finally, the shortening of the C–C bond and elongation of C–N bonds within the diimine moiety from 1.461 to 1.410 Å and from 1.310 to 1.347 Å, respectively are clearly consistent with an increase in bond order for the C–C bond and a decrease in bond order for the C–N bonds, as expected for a reduction of the bian ligand (compare with Scheme 1). All

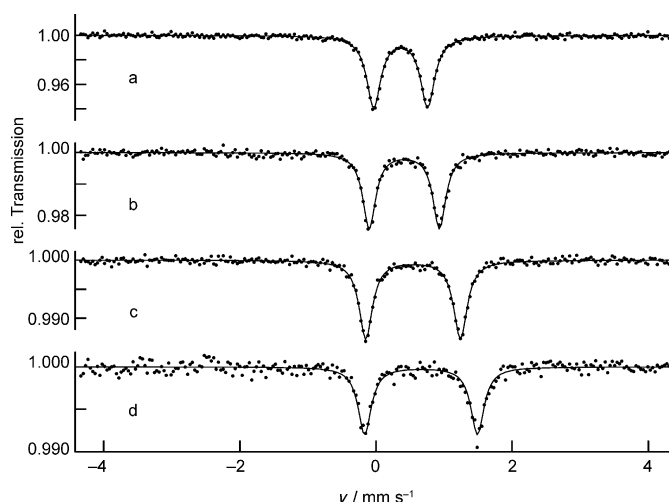
of these observations derived from the structural analysis support the description of the reduced complex at 150 K as a low-spin iron(II) complex coordinated to the  $\pi$ -radical ligand  $\text{bian}^{1-}$ . This assignment is corroborated by the ESR spectrum of a frozen solution of **3** in DMF containing 0.2 M tetrabutylammonium perchlorate (Figure 2). The rhombic



**Figure 2.** X-Band EPR spectrum of **3** in 0.2 M solution of TBAP in DMF at 77 K; a) experimental, b) simulated. TBAP = tetrabutylammonium perchlorate.

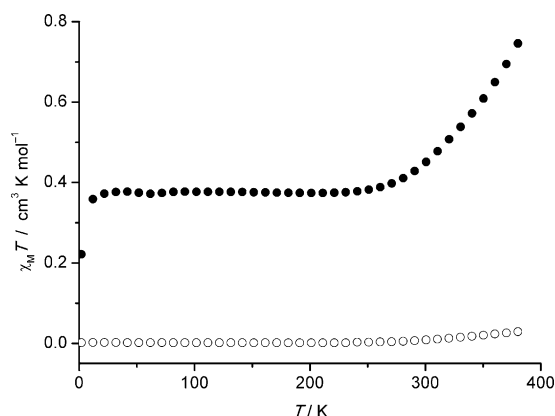
signal with  $g$  values at 2.0056, 1.9984, and 1.9804 indicates an  $S = 1/2$  ground state for the complex. The rather small anisotropy of the rhombic signal and the quintet splitting of the low field  $g$  component with a hyperfine coupling constant of 35.66 MHz owing to the interaction between the electron spin and the nuclear spin ( $I = 1$ ) of two nitrogen atoms are consistent with the formulation as a  $\pi$ -radical anion  $\text{bian}^{1-}$  coordinated to a diamagnetic low-spin iron(II) ion. The deviation of the average  $g$  value of the coordinated  $\pi$ -radical ( $g_{\text{av.}} = 1.9948$ ) compared to the tetraisopropyl derivative of the radical ligand coordinated to a lithium ion ( $g_{\text{av.}} = 2.0021$ )<sup>[5d]</sup> suggests substantial amounts of  $\pi$ -interactions between the spin orbitals of the radical ligand and the  $t_{2g}$  d-orbitals of the metal ion. The Mössbauer spectrum of **3** at 70 K (Figure 3) shows a quadrupole doublet with  $\delta_{\text{IS}} = 0.36 \text{ mm s}^{-1}$  and  $\Delta E_{\text{Q}} = 0.80 \text{ mm s}^{-1}$ , confirming the low-spin state of the iron(II) ion. The significant decrease in size of the quadrupole splitting constant is interpreted as an indication that the influence of the diminished  $\pi$ -acceptor strength of the reduced ligand on the Mössbauer parameters is stronger than the influence of the increased  $\sigma$ -donor strength.

The temperature-dependent measurements demonstrate unambiguously that **3** undergoes a SCO transition when the temperature is raised. Thus, an increase of all Fe–N bond lengths is observed with increasing temperatures. At 383 K (at even higher temperatures the SCO is no longer reversible),<sup>[12]</sup> the average Fe–N<sub>py</sub> and Fe–N<sub>amine</sub> bond lengths of 2.067 and 2.238 Å, respectively, demonstrate that the SCO process to the high-spin state is incomplete.<sup>[4]</sup> The increase of the average Fe–N<sub>bian</sub> bond length from 1.998 Å at 150 K to 2.074 Å at 383 K is considerably smaller than that of the other



**Figure 3.** Mössbauer spectra of solid **3** at a) 70 K, b) 298 K, c) 333 K, and d) 383 K.

Fe–N bond lengths. Further, the C–C and C–N bond lengths within the diimine unit confirm that the radical anion nature of  $\text{bian}^{1-}$  is preserved. Magnetic susceptibility data were measured by a SQUID magnetometer at temperatures ranging from 2 to 380 K (Figure 4). After an initial increase



**Figure 4.** Variation of the product  $\chi_{\text{M}}T$  with temperature a) for solid **3** (●; data have been corrected for residual high-spin fraction (“paramagnetic impurities” with  $S = 3/2$ ) and temperature-independent paramagnetism ( $6.9 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ ); see the Supporting Information for details) and b) for solid **2** (○; data have been corrected for temperature-independent paramagnetism ( $3.6 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$ )) at an applied magnetic field of 0.5 T.

from  $0.22 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K to  $0.37 \text{ cm}^3 \text{ K mol}^{-1}$  at 22 K, the value of  $\chi_{\text{M}}T$  remains constant until 240 K, indicating that the  $S = 1/2$  ground state arising from the diamagnetic low-spin ion and the paramagnetic coordinated radical ligand prevails up to this temperature. Above 240 K, SCO commences and  $\chi_{\text{M}}T$  rises to a value of  $0.75 \text{ cm}^3 \text{ K mol}^{-1}$  at 380 K, confirming that the SCO is not complete at this temperature.<sup>[13]</sup> Generally, compared to the solid state, the SCO equilibrium of the dissolved complex at the same temperature is shifted more to the high-spin state. The  $\chi_{\text{M}}T$  value of  $2.13 \text{ cm}^3 \text{ K mol}^{-1}$  of the dissolved complex at 300 K, determined by NMR spectroscopy

copy using Evans' method,<sup>[14]</sup> is consistent with a high-spin iron(II) ion ( $S=2$ ) that is strongly antiferromagnetically coupled to the coordinated ligand radical ( $S=1/2$ ) resulting in an  $S=3/2$  state whose  $\chi_M T$  value deviates from the spin-only value because of spin-orbit coupling. The  $\chi_M T$  value of the solution remains constant between 300 and 350 K indicating that the excited  $S=5/2$  state is not populated at these temperatures. Further, no evidence is found for the occurrence of SCO in solution. Therefore, these solution data can be interpreted that either the dissolved complex occupies a high-spin state without being involved in a SCO or alternatively that SCO of **3** takes place in solution, but is already completed at this temperature. SCO is also supported by the temperature-dependent Mössbauer spectra of **3** (Figure 3, Table 2). The doublet at 383 K, with  $\delta_{IS} =$

**Table 2:** Mössbauer parameters for **3**.

$T/K$	$\delta_{IS}/\text{mm s}^{-1}$	$\Delta E_Q/\text{mm s}^{-1}$
70	0.36	0.79
200	0.36	0.80
298	0.41	1.03
333	0.55	1.39
383	0.66	1.66

$0.66 \text{ mm s}^{-1}$  and  $\Delta E_Q = 1.67 \text{ mm s}^{-1}$ , already indicates a sizable contribution from the high-spin state. It is interesting to note that, in contrast to the usual observation of two distinct doublets (corresponding to the low-spin and the high-spin iron(II) ions) in all iron(II) SCO processes known to occur below 300 K, only one doublet is detected for **3** at all temperatures. This indicates that the SCO transition in **3** occurs considerably faster than the timescale of the Mössbauer experiment, implying a rate exceeding  $10^7$  to  $10^8 \text{ s}^{-1}$ . The SCO process in **3** takes place at temperatures higher than 300 K. Therefore, this fast interconversion may be explained by the general growth of any reaction rate with increasing temperatures, leading to a broadening of the signals and, eventually, to a coalescence of the two quadrupole doublets to a single averaged doublet in Mössbauer spectra recorded above 300 K. An alternative explanation is based on the fact, that the SCO in **3** occurs between an  $S=1/2$  and an  $S=3/2$  state. Owing to the reduced spin difference  $\Delta S=1$ , a larger spin-orbit interaction between the low-spin and high-spin electronic states would be expected to be present, thereby leading to an increase in the SCO interconversion rate. A similar interpretation based on increased spin-orbit interactions has been put forward as an explanation for a high interconversion rate (above 300 K) observed for a SCO of a distorted iron(II) complex.<sup>[15]</sup> At this point in time, we cannot rule out either of these two explanations or estimate the relative effect that each factor exerts on the interconversion rate.

To summarize our results, the reduction of a coordinated  $\pi$ -acceptor ligand leads to a radical anion with a weaker ligand field strength. This suggests that the weakening effect on the  $\pi$ -acceptor properties of the radical ligand by an additional electron in the  $\pi^*$ -orbital is more pronounced than

the strengthening effect on the  $\sigma$ -donor properties due to the additional negative charge. Spin crossover properties have been unequivocally established in an iron(II) complex where the metal ion is directly coordinated to a radical ligand. Radical ligand complexes displaying SCO properties are rare. There are some examples of SCO iron(III) complexes available;<sup>[16]</sup> recently we have reported on a SCO cobalt(II) semiquinone complex.<sup>[9]</sup> With respect to iron(II) complexes, to the best of our knowledge, only two iron(II) radical complexes that exhibits SCO properties have been reported.<sup>[17]</sup> However, in the first example, two reduced tetracyanoquinodimethane units are axially coordinated to an iron(II) ion.<sup>[17a]</sup> Because of strong intermolecular antiferromagnetic interactions between the coordinated radical ligands of neighboring complexes in the solid, these radicals do not affect the magnetic properties of the metal ion, nor do they exert any substantial electronic influence on the SCO properties of the iron ion, that is, a SCO from an  $S=0$  to an  $S=2$  state is found with similar interconversion rates, as observed in other iron(II) complexes with SCO below 300 K which contain no radical ligand. In the second reported SCO iron(II) radical complex, the radical is not directly coordinated to the iron(II) ion, but is instead located on the periphery of the ligand, and only weak magnetic interactions are observed between the spins of the radical and the high-spin iron(II) ion.<sup>[17b]</sup> In contrast, the coordinated radical ligand in **3** displays strong magnetic interactions with the iron ion and influences the magnetic properties of the complex to a significant extent. Thus, SCO is observed between an  $S=1/2$  and an  $S=3/2$  state. It is expected that the reduced spin difference  $\Delta S=1$  leads to a larger spin-orbit interaction between the low-spin and high-spin electronic states and, therefore, to an increase in the SCO interconversion rate. At the moment we cannot however provide any unambiguous experimental evidence for this SCO accelerating effect. Finally, this investigation demonstrates that SCO properties can be switched on or off through a control of the redox state of a coordinated ligand.

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- [18] CCDC 990900 (**1**), 990901 (**3**, 150 K), 990902 (**3**, 293 K), 990903 (**3**, 383 K), and 990899 (bian) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).