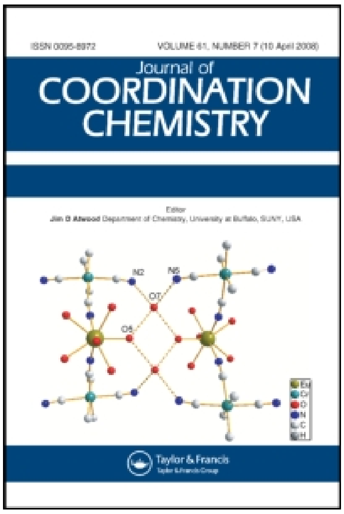

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High-spin iron(III) complexes: structural, spectroscopic, and photochemical studies

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High-spin iron(III) complexes: structural, spectroscopic, and photochemical studies

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Reaction of $FeCl_3$ with one equivalent of acac (acac = pentane-2,4-dionate) and KTp^{Me2} (Tp^{Me2} = hydrotris(3,5-dimethyl-pyrazol-1-yl)borate) yielded $Tp^{Me2}Fe(acac)Cl$ (**3**), which upon reaction with methanolic solution of sodium azide resulted in the formation of a six coordinate compound $Tp^{Me2}Fe(acac)N_3$ (**4**) with a single azide. When the reaction of $FeCl_3$ and KTp^{Me2} was performed with two equivalents of sodium azide and one equivalent of 3,5-dimethylpyrazole ($Pz^{Me2}H$), a six coordinate *cis* azide compound $[Tp^{Me2}Fe(Pz^{Me2}H)(N_3)_2]$ (**5**) was obtained. These compounds were characterized by spectroscopic methods and single crystal X-ray crystallography. Electrochemical studies of **5** show that it can be irreversibly reduced at relatively lower potential than **4**. The photolysis of **5** was performed at 77 K at different wavelengths (480, 419, and 330 nm) showing that **5** was photoreduced to a high-spin Fe(II) species instead of photooxidized to Fe(V).

Keywords: Mononuclear iron complex; Pyrazolylborate; Azide ligand; Crystal structure

1. Introduction

Coordination chemistry in high-valent iron is of considerable interest due to their important role in biological systems viz. in heme or different nonheme metalloenzymes [1, 2]. The majority of iron(IV)-containing complexes utilize bridging [3] or terminal [4] oxo ligands; high-valent iron compounds without oxo groups are very scarce [5–7]. The first spectroscopic evidence for high-valent iron(V) nitrido was reported in frozen matrix experiments. Wagner and Nakamoto [8] reported resonance Raman study of an octaethylporphyrinato nitride (OEP)Fe(V)N formed via photochemically induced N_2 liberation from a coordinated azide. Meyer *et al.* [9] applied similar photochemical strategy on low-spin iron azido compound with cyclam-type ligand to generate a high-valent iron [Fe(V)nitrido]. Song *et al.* [10] reported the synthesis of high-spin Fe(III) azide compounds with pentadentate ligands containing the 1,4,7-triazacyclononane-1,4-diacetate motif and suggested that high-spin Fe(III) azide cannot be used for the preparation of the corresponding iron(V) nitrido. These studies clearly indicate that the nature of ligands play very important roles in photolysis of Fe(III) azide compounds.

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Tris(pyrazolyl)borates have been widely used as supporting ligands for various inorganic and organometallic compounds as well as in bioinorganic model compounds, but their uses in preparation of high-valent transition metal nitrides is very limited [11]. In the present article, we have applied methyl-substituted hydrotris(pyrazolyl)borate for preparation of new Fe(III) octahedral complexes containing chloro, azido, or bis-azido ligands. The bis-azido Fe(III) compound has been examined for photolysis in a frozen state for the generation of iron(V) nitride species; no evidence for photo-oxidation to Fe(V) has been obtained but formation of Fe(II) species was observed.

2. Experimental

2.1. *Materials*

All solvents were purified by literature methods [12]. Reagents of highest grade commercially available were used without purification. All reactions were carried out under nitrogen using standard Schlenk tube techniques unless otherwise stated. 3,5-Dimethylpyrazole [$Pz^{Me2}H$] **1** and sodium acetylacetonate (acac) were purchased from Aldrich Chemical Company, Germany. Potassium hydrotris(3,5-dimethyl-pyrazol-1-yl)borate [KTp^{Me2}] **2** was synthesized by literature methods [13].

2.2. *Synthesis of complexes*

2.2.1. [Tp^{Me2}Fe(acac)Cl] (3). Methanolic solution of Fe(III) chloride hexahydrate (0.164 g, 0.62 mmol) and sodium acetylacetonate (0.075 g, 0.62 mmol) was stirred for 1 h. Then dichloromethane (10 mL) solution of KTp^{Me2} (0.180 g, 0.54 mmol) was added and the resultant solution was stirred for an additional 2 h. The reaction mixture was filtered over Celite, evaporated to dryness and recrystallized from acetonitrile. Suitable single crystals for X-ray data collection was obtained at −20°C. Yield: 0.192 g (73%). Anal. Calcd (%) for $C_{20}H_{29}N_6O_2BClFe$ (**3**): C, 49.23; H, 5.94; N, 17.23. Found: C, 49.03; H, 5.76; N, 17.11. IR (KBr, cm^{-1}): 2547 ν(BH), 1623 ν(CO). UV-Vis (MeCN, nm, ε $M^{-1}cm^{-1}$): 283 (1868), 527 (152). Magnetic moment (290 K): 5.91 B.M.

2.2.2. [$Tp^{Me2}Fe(acac)N_3$] (4). Methanolic solution of sodium azide (0.034 g, 0.52 mmol) was added to the acetonitrile (10 mL) solution of **3** (0.315 g, 0.52 mmol) and the mixture was stirred for 1 h. The resultant solution was filtered over Celite and dried under vacuum. The compound was recrystallized from a mixture of *n*-pentane/dichloromethane and suitable crystals for X-ray data collection were obtained at −20°C. Yield: 0.174 g (68%). Anal. Calcd (%) for $C_{20}H_{29}N_9O_2BFe$ (**4**): C, 48.58; H, 5.87; N, 25.50. Found: C, 48.43; H, 5.64; N, 25.23. IR (KBr, cm^{-1}): 2541 ν(BH), 2058 $\nu(N_3)$, 1629 ν(CO). UV-vis (MeCN, nm, ε $M^{-1}cm^{-1}$): 289 (1952), 440 (684), 581 (168). Magnetic moment (290 K): 5.91 B.M.

2.2.3. [$Tp^{Me2}Fe(Pz^{Me2}H)(N_3)_2$] (5). Compound **5** was synthesized by reaction of Fe(III) chloride (0.210 g, 0.78 mmol), KTp^{Me2} (0.262 g, 0.78 mmol), $Pz^{Me2}H$ (0.074 g, 0.78 mmol), and sodium azide (0.101 g, 1.56 mmol) in 30 mL methanol.

The reaction mixture was refluxed for 2 h, filtered over Celite and the solvent evacuated to dryness under vacuum. Crystallization from CH_3CN (5 mL) at −20°C led to the formation of suitable crystals for X-ray data collection. Yield: 0.274 g (66%). Anal. Calcd (%) for $C_{20}H_{30}N_{14}BFe$ (**5**): C, 45.02; H, 5.62; N, 36.77. Found: C, 45.23; H, 5.44; N, 36.54. IR (KBr, cm^{-1}): 2540 ν(BH), 2052 $\nu(N_3)$. UV-Vis (MeCN, nm, ε $M^{-1}cm^{-1}$): 284 (1987), 442 (697), 574 (171). Magnetic moment (290 K): 5.93 B.M.

2.3. *Physical measurements*

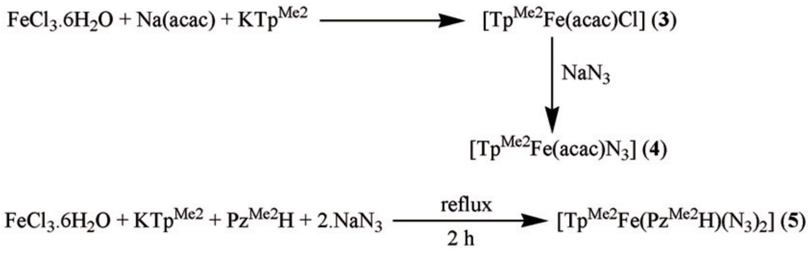
Carbon, hydrogen, and nitrogen were analyzed with a Vario EL III elemental analyzer after carefully drying samples under vacuum for several hours. UV-Vis spectra were recorded on a Perkin–Elmer Lambda 35 UV-vis spectrophotometer. IR spectra were obtained on a Thermo Nikolet Nexus FT-IR spectrometer in KBr. Room temperature magnetic susceptibility measurements were done on a Princeton Applied Research vibrating sample magnetometer Model 155 and magnetic susceptibility measurements at variable temperature (2–300 K) were performed on a Quantum Design SQUID Magnetometer Model MPMS. Cyclic voltammetry was performed using an EG&G potentiostat/galvanostat Model 273A for acetonitrile solution of samples containing 0.10 M $[N(n\text{-}Bu)_4]PF_6$ as supporting electrolyte. Ferrocene was used as an internal standard and all reported potentials are referenced *versus* the Fc^+/Fc couple. Mössbauer data were recorded on an alternating constant-acceleration spectrometer. The minimum experimental line width was 0.24 mm s^{-1} (full width at half-height). The field at the sample is oriented perpendicular to the γ-beam. The $^{57}Co/Rh$ source (1.8 GBq) was positioned at room temperature inside the gap of the magnet system at a zero-field position. Isomer shifts are quoted relative to iron metal at 300 K.

2.4. *X-ray crystallography*

The X-ray data collection and processing for **3**–**5** were performed on a Bruker Kappa Apex – CCD diffractometer by using graphite monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å) at 100 K. Crystal structures were solved by direct methods. Structure solution, refinement, and data output were carried out with SHELXTL [14, 15]. Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model. Images were created with DIAMOND [16].

3. Results and discussion

Complex **3** was prepared by reaction of ferric chloride with potassium hydrotris(3,5-dimethyl-pyrazol-1-yl)borate and sodium acetylacetonate in 1 : 1 : 1 ratio (scheme 1). The monoazide bonded iron complex, **4**, was prepared by reaction of **3** with one equivalent of sodium azide in a mixture of acetonitrile and methanol. When the reaction of ferric chloride, KTp^{Me2}, and two equivalents of sodium azide was performed in the presence of free 3,5-dimethylpyrazole, we got a bis(azide) species in cis geometry at room temperature and on refluxing. Reaction of cis-$[Fe^{III}(cyclam)Cl_2]Cl$ with sodium



Scheme 1. Synthesis of complexes **3**–**5**.

azide [9] yielded the *cis* azide system at −18°C and *trans* azide system at 50°C. However, in the present case the product is always *cis* irrespective of the temperature of reaction medium, showing the influence of methyl-substituted pyrazolylborate as supporting ligand in place of cyclam.

3.1. *Spectroscopic studies*

Complex **3** showed a decrease in wavenumber of the carbonyl stretching band of the acac ligand from 1710 to 1623 cm^{-1} upon complexation with metal ions [17] and also showed B–H stretching band at 2547 cm^{-1}, suggesting binding of Tp^{Me2}. In the IR spectrum of **4**, the band at 2058 cm^{-1} confirmed the terminal binding of azide [18]. In **5**, the binding of Tp^{Me2} was suggested as the position of B–H band shifted to higher wave number (2540 cm^{-1}) from 2480 cm^{-1} (free Tp^{Me2}) and this complex also showed a band at 2052 cm^{-1} due to terminal azide. UV-Vis spectra of **4** and **5** in acetonitrile at room temperature contain azide-to-Fe charge-transfer bands in the range 440–442 nm [9]. This band is absent in **3** due to the presence of chloride in place of azide. Compounds **4** and **5** are high-spin like other reported compounds with 1,4,7-triazacyclononane-1,4-diacetate motif [10].

3.2. *Crystallographic studies*

Structures of **3**–**5** at 100 K have been determined by a single-crystal X-ray diffraction. Crystallographic data are summarized in table 1 and selected bond lengths and angles are given in table 2. Compound **3** crystallizes in the triclinic system with $Z = 2$ as a neutral complex containing a terminal chloro with octahedrally coordinated Fe(III). As shown in figure 1, the terminal chloro is *trans* to N of the pyrazole. The acac is a coordinated bidentate. Average Fe–N and Fe–O bond lengths are 2.134 and 1.985 Å, respectively. The chloro is 2.364(16) Å from Fe, in the range of reported trans-chloro complexes [19–21].

Crystal structures of the Fe(III)-chloro and single azide bonded Fe(III)-azido complex (figure 2) are similar. Both structures contain the ferric ion in slightly trigonally distorted octahedral environment, as evidenced by N–Fe–O and N–Fe–X_{axial} angles larger than 100°. Each nitrogen of Tp^{Me2} is unique in its coordination to iron; therefore, the Fe–N(Tp^{Me2}) distances in **3** and **4** are all slightly different, though all are around 2.135 ± 0.027 Å.

The structure of **5** (figure 3) is similar to **3** and **4** except that in place of acac, in **5**, the coordination is completed by nitrogen $Pz^{Me2}H$ and one more azide. The Fe–N bond

Table 1. Crystallographic data and refinement parameters of **3** · CH_3CN, **4** · CH_2Cl_2 and **5** · CH_3CN.

	3 · CH_3CN	**4** · CH_2Cl_2	**5** · CH_3CN
Empirical formula	$C_{22}H_{32}N_7O_2BClFe$	$C_{21}H_{31}N_9O_2BCl_2Fe$	$C_{22}H_{32}N_{15}BFe$
Formula weight	528.66	579.11	573.29
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	Pbca
Unit cell dimensions (Å, °)			
a	8.090(5)	8.107(5)	19.946(5)
b	11.140(5)	11.738(5)	17.439(5)
c	15.090(5)	14.643(5)	15.807(5)
α	104.170(5)	100.779(5)	90.00(5)
β	93.000(5)	91.280(5)	90.00(5)
γ	100.190(5)	98.175(5)	90.00(5)
V (Å^3)	1291.2(11)	1353.2(11)	5498(3)
Z	2	2	8
D_{calcd} (mg m^{-3})	1.360	1.421	1.385
Absorption coefficient (mm^{-1})	0.720	0.791	0.591
$F(000)$	554	602	2400
Crystal size (mm^3)	0.29 × 0.17 × 0.15	0.26 × 0.18 × 0.16	0.26 × 0.18 × 0.11
θ Range for data collection (°)	1.40–27.35	1.42–26.51	1.78–28.45
Index ranges	$-10 \le h \le 10$	$-10 \le h \le 10$	$-26 \le h \le 26$
	$-14 \le k \le 14$	$-14 \le k \le 14$	$-23 \le k \le 23$
	$-19 \le l \le 19$	$-18 \le l \le 18$	$-21 \le l < 21$
Reflections collected	5856	5619	6936
Independent reflections (R_{int})	3432 (0.0461)	2806 (0.0318)	5788 (0.0412)
Completeness to $2\theta = 50°$ (%)	98.9	99.0	99.8
Data/restraints/parameters	3432/0/320	2806/0/337	5788/0/227
Goodness-of-fit on F^2	1.058	1.091	1.060
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0509$	$R_1 = 0.0692$	$R_1 = 0.0899$
	$wR_2 = 0.1472$	$wR_2 = 0.1762$	$wR_2 = 0.1879$
R indices (all data)	$R_1 = 0.0795$	$R_1 = 0.0887$	$R_1 = 0.0925$
	$wR_2 = 0.1812$	$wR_2 = 0.1988$	$wR_2 = 0.1982$
Largest difference in peak and hole (e Å^{-3})	0.56 and −0.95	1.31 and −0.92	1.32 and −0.98

distance of coordinated $Pz^{Me2}H$ [2.142(12) Å] is smaller than the Fe–N bond distances of coordinated Tp^{Me2} (table 2). The Fe–N bond lengths of coordinated azide in **4** and **5** (about 1.990 Å) are typical for Fe(III) azido complexes [9, 10, 22].

3.3. *Electrochemistry and photolysis study*

The electrochemistry of **4** and **5** in acetonitrile have been studied by cyclic and square-wave voltammetry as shown in figures S6 and S7. Redox potentials were calculated with reference to ferrocene/ferrocenium couple. The chloro complex was also studied but only irreversible waves were observed. The azido complexes show two important electrochemical processes: a one-electron reduction at −623 and −707 mV and a one-electron oxidation at 1305 and 698 mV for **4** and **5**, respectively, all fully irreversible. The reduction and oxidation potential of **5** are lower than other high-spin azido complexes [4a, 23].

On the basis of relatively small redox potential, the photolysis of the powder sample of **5** (50.0 mg) was performed frozen in liquid nitrogen with a Rayonet photochemical reactor (RPR-100) equipped with 480, 419, and 330 nm tubes hoping to form high-valent iron-nitride compounds. Samples for photolysis at 77 K were prepared via the

Table 2. Selected bond lengths (Å) and angles (°) for **3**, **4**, and **5**.

$[Tp^{Me2}Fe(acac)Cl]$ (**3**)			
Fe(1)–N(1)	2.131(4)	Fe(1)–N(2)	2.107(4)
Fe(1)–N(3)	2.164(4)	Fe(1)–O(1)	1.987(4)
Fe(1)–O(2)	1.983(4)	Fe(1)–Cl(1)	2.364(16)
N(1)–Fe(1)–N(2)	91.39(16)	N(1)–Fe(1)–N(3)	82.87(16)
N(1)–Fe(1)–O(1)	90.91(15)	N(1)–Fe(1)–O(2)	175.10(15)
N(1)–Fe(1)–Cl(1)	91.14(12)	N(2)–Fe(1)–N(3)	83.90(16)
N(2)–Fe(1)–O(1)	174.74(14)	N(2)–Fe(1)–O(2)	89.85(15)
N(2)–Fe(1)–Cl(1)	92.35(12)	N(3)–Fe(1)–O(1)	91.70(15)
N(3)–Fe(1)–O(2)	92.55(15)	N(3)–Fe(1)–Cl(1)	172.84(12)
O(1)–Fe(1)–O(2)	87.47(15)	O(1)–Fe(1)–Cl(1)	92.33(11)
O(2)–Fe(1)–Cl(1)	93.54(11)		
$[Tp^{Me2}Fe(acac)N_3]$ (**4**)			
Fe(1)–N(1)	2.131(5)	Fe(1)–N(2)	2.134(5)
Fe(1)–N(3)	2.122(5)	Fe(1)–N(4)	1.995(5)
Fe(1)–O(1)	1.988(4)	Fe(1)–O(2)	1.986(4)
N(1)–Fe(1)–N(2)	84.31(19)	N(1)–Fe(1)–N(3)	84.72(19)
N(1)–Fe(1)–N(4)	174.70(2)	N(1)–Fe(1)–O(1)	91.95(18)
N(1)–Fe(1)–O(2)	92.71(18)	N(2)–Fe(1)–N(3)	88.69(19)
N(2)–Fe(1)–N(4)	91.10(2)	N(2)–Fe(1)–O(1)	91.52(19)
N(2)–Fe(1)–O(2)	176.71(18)	N(3)–Fe(1)–N(4)	92.50(2)
N(3)–Fe(1)–O(1)	176.63(18)	N(3)–Fe(1)–O(2)	92.45(18)
N(4)–Fe(1)–O(1)	90.90(2)	N(4)–Fe(1)–O(2)	92.00(2)
O(1)–Fe(1)–O(2)	87.16(1)		
$[Tp^{Me2}Fe(Pz^{Me2}H)(N_3)_2]$ (**5**)			
Fe(1)–N(1)	2.137(12)	Fe(1)–N(2)	2.112(12)
Fe(1)–N(3)	2.171(12)	Fe(1)–N(4)	2.142(12)
Fe(1)–N(5)	1.985(17)	Fe(1)–N(6)	1.972(16)
N(1)–Fe(1)–N(2)	85.4(5)	N(1)–Fe(1)–N(3)	83.6(4)
N(1)–Fe(1)–N(4)	170.0(5)	N(1)–Fe(1)–N(5)	94.1(5)
N(1)–Fe(1)–N(6)	95.4(5)	N(2)–Fe(1)–N(3)	86.5(5)
N(2)–Fe(1)–N(4)	87.0(5)	N(2)–Fe(1)–N(5)	178.6(5)
N(2)–Fe(1)–N(6)	91.6(5)	N(3)–Fe(1)–N(4)	89.6(5)
N(3)–Fe(1)–N(5)	92.2(5)	N(3)–Fe(1)–N(6)	177.9(6)
N(4)–Fe(1)–N(5)	93.5(5)	N(5)–Fe(1)–N(6)	89.6(6)

previously described method [9] and photolysis was performed on a stirred suspension of a fine snow of **5** in liquid nitrogen. Since the photolysis products of azido-manganese complexes have been shown to be wavelength dependent [24], we performed the photochemistry of **5** using both visible (480, 419 nm) and UV (330 nm) light. After photolysis of the azide complex for 6 h, the color of the snow became darker and a portion of the photolyzed snow was packed in a Mössbauer cup for analysis.

3.4. *Mössbauer measurements*

The results of zero-field Mössbauer measurements of **5** are listed in table 3. Before photolysis, the isomer shift of **5** was 0.58 mm s^{-1} and quadrupole splitting was 0.62 mm s^{-1} (figure S8), typical for high-spin octahedral Fe(III) complexes and reflecting the high symmetry of the high-spin d^5 electron configuration [9].

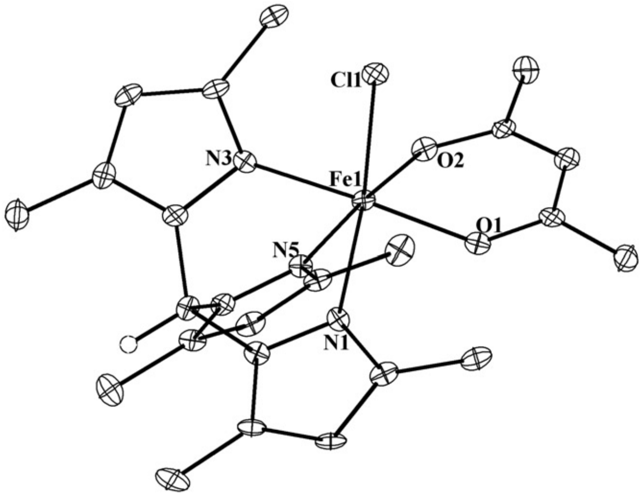


Figure 1. Molecular structure of [Tp^{Me2}Fe(acac)Cl] (**3**). Hydrogen atoms and solvent molecule have been omitted for clarity.

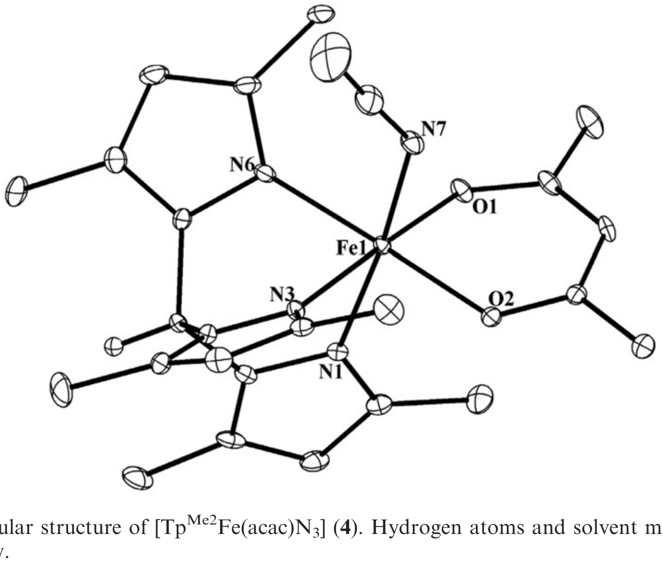


Figure 2. Molecular structure of [Tp^{Me2}Fe(acac)N$_3$] (**4**). Hydrogen atoms and solvent molecule have been omitted for clarity.

The zerofield Mössbauer spectrum (80 K, figure 4) of **5** after photolysis showed new signal at isomer shift of $1.13\,\mathrm{mm\,s^{-1}}$ and quadrupole splitting of $3.51\,\mathrm{mm\,s^{-1}}$, indicating the formation of high-spin iron(II) compound upon photoreduction accounting for 34% of the spectral intensity. The signal for the presence of Fe(V) could not be observed in Mössbauer spectrum. The Mössbauer parameters of the photoreduced product are comparable to those of similar high-spin Fe(II) compounds [9, 23]. The remaining 66% of intensity is fitted to the Fe(III) high spin ($\delta = 0.49\,\mathrm{mm\,s^{-1}}$, $\Delta E_Q = 0.82\,\mathrm{mm\,s^{-1}}$), most likely as starting sample.

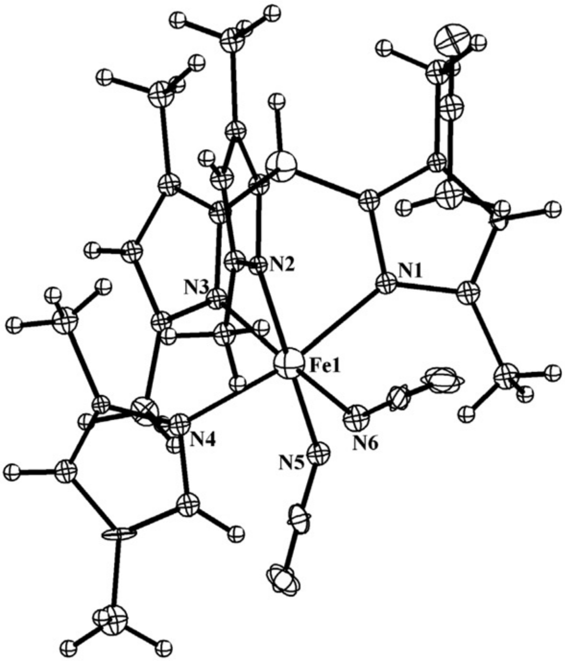


Figure 3. Molecular structure of $[Tp^{Me2}Fe(Pz^{Me2}H)(N_3)_2]$ (**5**). Hydrogen atoms and solvent molecule have been omitted for clarity.

Table 3. Zero-field Mössbauer parameters for $[Tp^{Me2}Fe(Pz^{Me2}H)(N_3)_2]$.

Complex	δ (mm s^{-1})	ΔE_Q (mm s^{-1})
5 (Before photolysis)	0.58	0.62
5 (After photolysis)	0.49[a]	0.82
	1.13[b]	3.51

[a] Fe(III) species; [b] Fe(II) species.

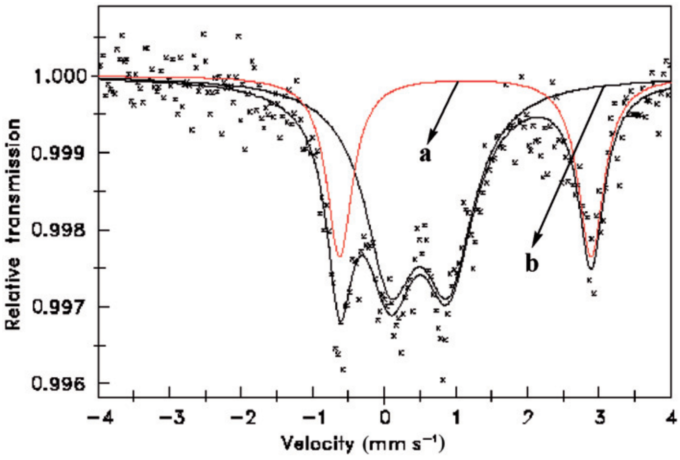


Figure 4. Zero-field Mössbauer spectra measured at 80 K for **5** after photolysis.

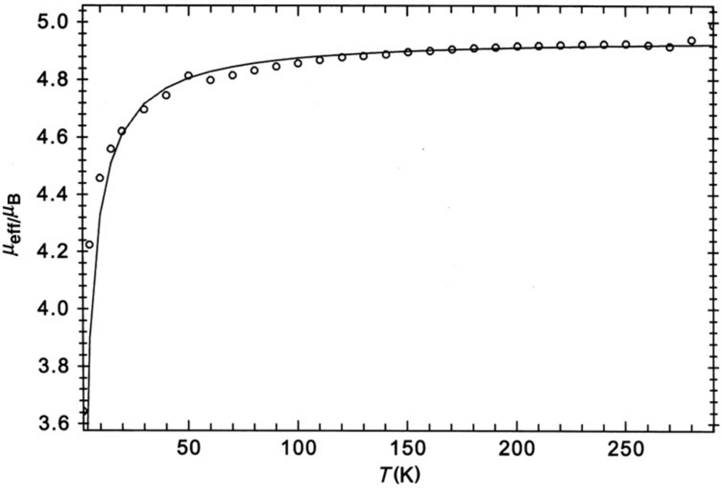


Figure 5. Temperature-dependence of the magnetic moment, μ_{eff}/μ_B of photolyzed product of **5**. The solid lines represent best fits to models described in the text; open circles are the experimental data.

3.5. *Magnetic measurements*

Magnetic moment values for **3**–**5** at 290 K are 5.91, 5.91, and 5.93 B.M., respectively, very close to the spin-only value for high-spin Fe(III) species ($S = 5/2$). The magnetic moment for photolyzed product of **5** shows slightly lower value i.e., 4.85 B.M., which can be attributed to presence of high-spin Fe(II) as shown in figure 5. The magnetic results also support our conclusion that the photolyzed product is Fe(II), not Fe(V).

4. Conclusions

We have reported three new Fe(III) high-spin complexes (**3**–**5**) having Tp^{Me2} as a supporting ligand. X-ray structures of these complexes revealed that three nitrogens in Tp^{Me2} coordinate facially to Fe(III) with two additional coordination sites occupied by acac in **3** and **4** and a chloride or azide anion; in **5**, acac is replaced by one $\text{Pz}^{\text{Me2}}\text{H}$ and one more azide cis to the other azide. Characterization of these complexes by magnetic susceptibility measurements and zero-field Mössbauer measurements are in good agreement with the high-spin Fe(III). Photolysis of **5** at 80 K shows the formation of photoreduced product having high-spin Fe(II) instead of photooxidized Fe(V) species. The present study supports the hypothesis that only low-spin Fe(III) azido complexes undergo photolysis with formation of iron(V)-nitrido, whereas high-spin complexes show photoreduction.

Supplementary material

The crystallographic data have been deposited with CCDC. Supplementary data are available from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request by quoting the deposition numbers CCDC reference numbers 660432–660434. E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Different noncovalent interactions, cyclic voltammogram, and Mössbauer spectrum can be seen from supplementary materials.

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