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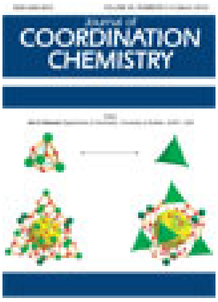

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Seven-coordinate iron(II) complexes of sulfur-based N_3S_2-macrocyclic ligands: synthesis, properties, and crystal structure

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Seven-coordinate iron(II) complexes of sulfur-based N_3S_2-macrocyclic ligands: synthesis, properties, and crystal structure

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The reaction of pyridine-2,6-dicarbaldehyde or 2,6-diacetylpyridine with 1,2-bis(*o*-aminophenylthio)ethane (**1**) in acetonitrile in the presence of stoichiometric amounts of iron(II) perchlorate gave the complexes $[(pyN_3S_2)Fe^{II}(ClO_4)_2]$ (**4**) and $[(pyN_3Me_2S_2)Fe^{II}(ClO_4)_2]$ (**5**) of the 15-membered N_3S_2 macrocyclic ligands, pyN_3S_2 = {6,7-dihydro-15,19-nitrilobenzo(*e*,*p*)(1,4,7,15)dithiadiazacyclo-heptadecine-*N*,*N*′,*N*″,*S*,*S*′} and $pyN_3Me_2S_2$ = {6,7-dihydro-16,18-dimethyl-15,19-nitrilobenzo(*e*,*p*)(1,4,7,15)dithiadiazacyclo-heptadecine-*N*,*N*′,*N*″,*S*,*S*′}, respectively. Physical measurements led to the conclusion that these complexes contained seven-coordinate iron(II) and a single-crystal X-ray examination of **4** confirmed this. Coordination of the Fe(II) center in **4** is best described as distorted pentagonal-bipyramidal with the three nitrogen atoms and two sulfur donors of the macrocycle defining the pentagonal plane and the perchlorate ions occupying axial positions. Room temperature (293 K) magnetic moments of **4** and **5** ($\mu_{eff} = 4.9$ and 4.7 B.M., respectively) are close to the value predicted for high-spin d^6 systems.

Keywords: Iron(II) complexes; Seven-coordinate; Macrocyclic ligands; Pentagonal-bipyramidal

1. Introduction

During the last decades a large number of complexes of macrocyclic pentadentate ligands which contain imine donors have been isolated from cyclic condensation reactions performed in the presence of metal ion templates [1]. The macrocyclic ligands 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16,-pentaene (abbreviated pydieneN_5) and 2,16-dimethyl-3,6,9,12,15,21-hexaazabicyclo[15.3.1]heneicosa-1(21),2,15,17,19-pentaene (abbreviated pydieneN_6) were the first macrocyclic ligands to be prepared which contained more than four donors [2]. A few years later, a second class of pentadentate macrocyclic ligands were prepared which, in addition to nitrogen donors, contain sulfur donors, and several metal complexes were

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isolated and characterized [3, 4]. Most of the isolated complexes were characterized as seven-coordinate, with the pentadentate macrocyclic ligand lying in a plane and with two monodentate anions occupying the axial positions. This was of interest because of the rarity of this stereochemistry among transition metal compounds, particularly those of the first row [5]. Some years later, Tasker *et al.* [1] reported a new series of ligands with intermediate rigidity which contain two benzo-linkages. One of them, illustrated in figure 1 (R=H), was isolated as its zinc complex. The study of pentadentate macrocyclic complexes with other transition metal ions, for example those with electron distributions that favor an octahedral coordination geometry, requires a macrocyclic ligand which is flexible and large enough to fold in order to provide a non-planar, five-donor arrangement. Such ligands and their iron(II) complexes are reported here. Very recently, a pentagonal-bipyramidal iron(II) complex of a related open-chain $pyN_3S_2Me_2$ ligand was reported by Nam *et al.* [6].

2. Experimental

2.1. *Materials*

All reagents and solvents used in this work were commercial products and of reagent quality unless otherwise stated. Pyridine-2,6-dicarbaldehyde, 2,6-diacetylpyridine and iron(II) perchlorate were obtained from Aldrich. Bis(2-aminophenylthio)ethane was synthesized as reported in the literature [7–10].

2.2. *Physical measurements*

Spectra were recorded on the following instruments: Infrared (IR) (KBr discs, solvent bands were compensated): Mattson Infinity instrument (60 AR) at $4\,cm^{-1}$ resolution from 400 to $4000\,cm^{-1}$; NMR: Jeol-JNM-GX 270, EX 270, and Lambda LA 400 with the protio-solvent signal used as an internal reference. Mass spectra: Jeol MSTATION 700 spectrometer; Elemental analyses: Carlo Erba EA 1106 or 1108 analyzer. The conductivity of the complexes was obtained using an industrial instrument model RC

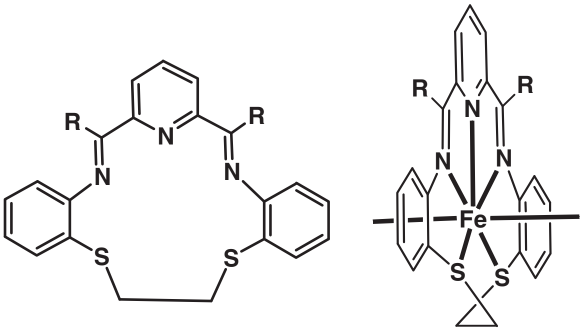


Figure 1. Schematic representation of the ligands **2** (R=H) and **3** ($R = CH_3$), and their iron(II) complexes **4** (R = H) and **5** ($R = CH_3$).

T68 Conductivity Bridge. Measurements were taken at room temperature at 1000 Hz on solutions that were $\sim 10^{-3}$ mol L^{-1}. Room-temperature magnetic susceptibilities of well-ground solid samples were measured by using a Cahn electro balance. Diamagnetic corrections for the ligands and counter ions were made using Pascal's constants [11]. Cyclovoltammetric (CV) measurements were performed in a one-compartment, three-electrode cell using a gold working electrode (Metrohm) with a geometrical surface of 0.7 cm^2 connected to a silver wire pseudo-reference electrode and a platinum wire serving as counter electrode (Metrohm). Measurements were recorded with an Autolab PGSTAT 30 unit at room temperature. The working electrode surface was cleaned using 0.05 µm alumina sonicated and washed with water every time before use. The working volume of 10 mL was deaerated by passing a stream of high purity N_2 through the solution for 15 min prior to the measurements and then maintaining an inert atmosphere of N_2 over the solution during the measurements. All CVs were recorded for the reaction mixture with a sweep rate of 50 mV s^{-1} at 25°C. Potentials were measured in 0.1 mol L^{-1} TBAP electrolyte solution and are reported *versus* an Ag/AgCl electrode.

2.3. *Synthesis*

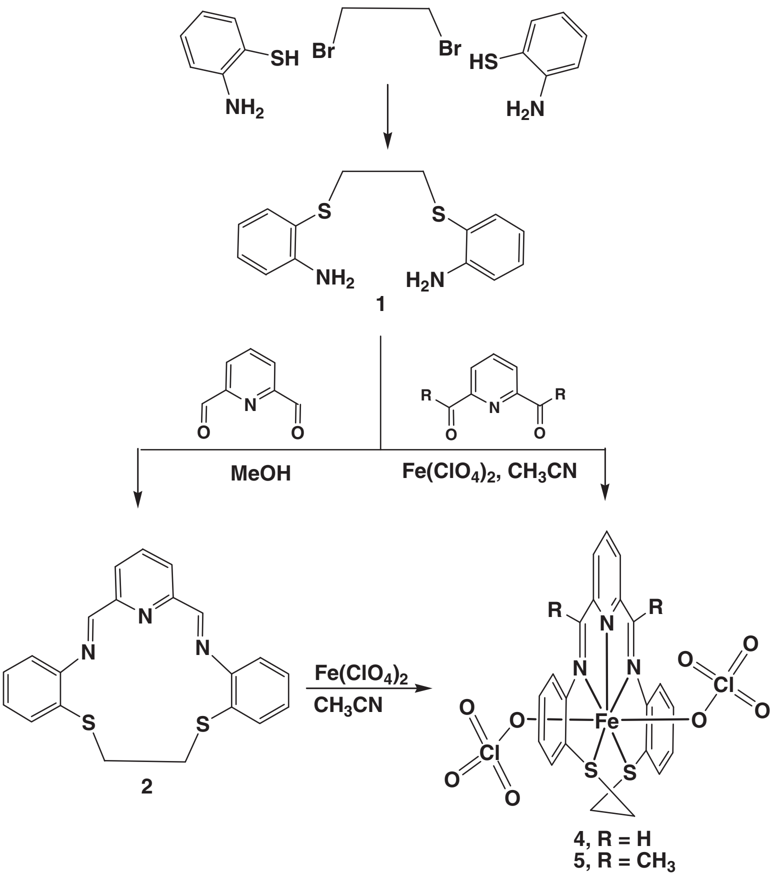
2.3.1. Preparation of the macrocyclic ligand pyN$_3$S$_2$ (2). The ligand pyN$_3$S$_2$ (**2**) was prepared according to the reactions presented in scheme 1. To a solution of **1** (0.307 g, 1.1 mmol) in EtOH (20 mL) was added, with continuous stirring, pyridine-2,6-dicarbaldehyde (0.150 g, 1.1 mmol). The mixture was stirred for about 10 min to give a yellow product, which was then filtered off and washed with EtOH. Yield of **2** (0.215 g, 68%). Anal. Calcd for $C_{22}H_{30.3}N_3O_{1.6}S_2$ (419.01): C, 62.98; H, 5.37; N, 10.02; S, 15.28. Found (%): C, 62.95; H, 5.54; N, 9.68; S, 15.00. IR (KBr, ν/cm^{-1}): 3066 (m, CH$_{\text{arom}}$), 2988 (m, CH$_{\text{aliph}}$), 1588 (s, C=N); MS (FD$^+$, CH_2Cl_2): $m/z = 376\,[M]^+$.

2.3.2. Preparation of the macrocyclic complex [(pyN$_3$S$_2$)Fe^{II}(ClO$_4$)$_2$] (4)

Caution: Metal perchlorate salts are potentially explosive and should be handled with care.

(a) *From 2*: To a solution of **2** (0.276 g, 1 mmol) in acetonitrile (20 mL) was added, with continuous stirring, a solution of $Fe(ClO_4)_2$ (0.280 g, 1.1 mmol) in acetonitrile (10 mL). The mixture was stirred for about 2 h to give a faint-green solution. Addition of diethyl ether (30 mL) leads to formation of green crystals of **4**. Yield 0.315 g (50%).

(b) *By template condensation*: Pyridine-2,6-dicarbaldehyde (0.135 g, 1 mmol), **2** (0.276 g, 1 mmol) and a slight excess (1.1–1.3 mmol) of iron(II) perchlorate were dissolved separately in methanol or acetonitrile. The solutions were mixed and stirred at room temperature for 5 h to give a green solution. The solution was concentrated to 5 mL under reduced pressure. Addition of diethyl ether leads to formation of a light green solid of **4** (0.423 g, 67%). Anal. Calcd for $C_{21}H_{17}Cl_2FeN_3O_8S_2$ (628.92): C, 40.02; H, 2.72; N, 6.67; S, 10.18. Found (%): C, 39.36; H, 3.22; N, 6.80; S, 9.65. $\mu_{\text{eff}} = 4.9$ B.M. IR (KBr, ν/cm^{-1}): 3092 (m, CH$_{\text{arom}}$), 2980 (m, CH$_{\text{aliph}}$), 1632 (s, C=N), 1596 (m, C=C), 1099, 624 (vs, perchlorate); MS (FD$^+$, MeOH): $m/z = 432$ $[M\text{-}2(ClO_4)_2]^+$.



Scheme 1. Synthesis of ligand **2** and the iron(II) complexes **4** and **5**.

2.3.3. Preparation of the macrocyclic complex [(pyMe$_2$N$_3$S$_2$)Fe^{II}(ClO$_4$)$_2$] (5). 2,6-Diacetylpyridine (0.163 g, 1 mmol), **2** (0.276 g, 1 mmol), and a slight excess (1.1–1.3 mmol) of iron(II) perchlorate were dissolved separately in acetonitrile. The solutions were mixed and stirred at 60°C for 2 h to give a grey solution. The solution was concentrated to 5 mL under reduced pressure. Addition of diethyl ether leads to formation of a grey solid of **5** (0.322 g, 47%). Anal. Calcd for $C_{29}H_{34}Cl_2FeN_4O_9S_2$ (772.05): C, 45.03; H, 4.43; N, 7.24; S, 8.29. Found (%): C, 45.28; H, 4.21; N, 6.84; S, 10.01. $\mu_{eff} = 4.7$ B.M. IR (KBr, ν/cm^{-1}): 3088 (m, CH$_{arom}$), 2973 (m, CH$_{aliph}$), 1609 (s, C=N), 1590 (m, C=C), 1094, 622 (vs, perchlorate); MS (FD$^+$, CH$_3$CN): $m/z = 460$ [M-2(ClO$_4$)$_2$]$^+$.

2.3.4. Crystal structure determination and refinement of 4. Brown plate-shaped single crystals of **4** were grown from layering of a saturated CH$_3$CN solution with diethyl ether at room temperature in the course of three days. A suitable single crystal was mounted on top of a glass capillary using protective perfluoropolyalkylether oil. Intensity data were collected on a Bruker-Nonius Kappa CCD diffractometer using

Table 1. Crystallographic data, data collection, and structure refinement details for **4**.

Empirical formula	$C_{21}H_{17}Cl_2FeN_3O_8S_2$
Formula weight	630.25
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	9.3024(3)
b	29.545(3)
c	8.9120(7)
α	90
β	105.346(3)
γ	90
Volume (Å^3), Z	2362.0(3), 4
Calculated density (g cm^{-3})	1.772
Absorption coefficient (mm^{-1})	1.098
F(000)	1280
Crystal size (mm^3)	0.39 × 0.20 × 0.05
θ range for data collection (°)	3.13–27.88
Reflections collected	66,252
Unique	5633
Observed [$I > 2\sigma(I)$]	4922
Max. and min. transmission	0.950 and 0.746
Data/restraints/parameters	5633/18/371
Goodness-of-fit on F^2	1.272
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0408$, $wR_2 = 0.1159$
R indices (all data)	$R_1 = 0.0488$, $wR_2 = 0.1191$
Final $\Delta\rho_{max/min}$ (e cm^{-3})	0.542/−0.448

Mo-Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). An empirical absorption correction based on multiple scans using SADABS was performed [12]. The structure was solved by direct methods and refined on F^2 using full-matrix least-squares procedures (SHELXTL NT 6.12) [13]. One of the coordinated perchlorates is disordered; two preferred orientations were refined resulting in site occupancies of 79.1(7)% for the major orientation (Cl2, O21–O23) and 20.9(7)% for the minor fraction (Cl2A, O21A–O23A). Hydrogen atoms were geometrically positioned and allowed to ride on the corresponding carrier atoms with their isotropic displacement parameter fixed at 1.2 or 1.5 times U_{eq} of the carbon. Table 1 summarizes selected crystallographic data, data collection, and structure refinement details.

3. Results and discussion

The iron(II) complexes, $[(pyN_3S_2)Fe^{II}(ClO_4)_2]$ (**4**) and $[(pyN_3Me_2S_2)Fe^{II}(ClO_4)_2]$ (**5**), were prepared by reacting the dialdehyde or diketone with 1,2-bis(*o*-aminophenylthio)ethane (**1**) in equimolar proportion in the presence of an equimolar concentration of the iron(II) perchlorate (see scheme 1 and the section 2 for further details). The addition of diethyl ether to the reaction solution afforded green crystals suitable for crystallographic analysis of **4**.

The macrocycle pyN$_2$RS$_2$, **2** (R = H), was isolated in the free form as a yellow solid when the reaction was repeated in the absence of iron perchlorate, whereas the macrocyclic pyN$_2$RS$_2$, **3** (R = CH$_3$), was isolated only as its iron complex. The latter reaction in the absence of iron perchlorate yielded only viscous oils suggestive of an oligomeric or polymeric constitution. IR spectra of this material showed an absorption at *ca* 1650 cm^{-1} characteristic of the –C=N– (imine) group, indicating that Schiff base condensation had occurred, but also a strong absorption at *ca* 1700 cm^{-1} characteristic of C=O, indicating the presence of residual keto-functions, presumably the terminal groups of open chain oligomers. The importance of the iron ion in promoting the cyclic condensation of the reactants and/or in stabilizing the macrocycle once formed is thus apparent [14]. This means that the synthesis was attempted but proved to be unsuccessful under the conditions employed. It is, of course, possible that the synthesis would be successful under different conditions. Attempts to isolate macrocycle **3** after displacement of the metal ion have so far proved to be unsuccessful, leading usually to regeneration of the diketone and diamine.

Evidence for the formation of the macrocycle comes from elemental analysis which is consistent with the condensation of dialdehyde or diketone, amine and iron(II) perchlorate in 1 : 1 : 1 molar ratio, and the X-ray structure determination of [(pyN$_3$S$_2$)Fe^{II}(ClO$_4$)$_2$] (**4**) (see later). IR spectra proved to be invaluable to confirm the presence of the imine-linkage at *ca* 1605–1632 cm^{-1}, but no absorption was found at *ca* 1700 cm^{-1} or at 3100–3300 cm^{-1}, which would occur if residual carbonyl or primary amine groups were present. In both complexes the ClO_4^- is coordinated as judged by the split nature of the ClO_4^- ν_3 and ν_4 bands at *ca* 1097 and *ca* 623 cm^{-1}. Further confirmation comes from the observation of a peak in the mass spectrum at $m/e = 432$ corresponding to [(pyN$_3$S$_2$)Fe^{II}]$^+$; no peaks of significant intensity were observed at higher m/e values. Room temperature (293 K) magnetic moments of both **4** and **5** of 4.9 and 4.7 B.M., respectively, are close to the value predicted for high-spin d^6 systems, in agreement with a S = 2 ground state. The rather high orbital contribution is consistent with the degeneracy of the d_{xz} and d_{yz} orbitals in D_{5h} symmetry [14].

Electrical conductivity measurements in acetonitrile show that both complexes are 1 : 2 electrolytes, indicating the displacement of the two perchlorates by acetonitrile such that the structure in acetonitrile could be formulated as [(chelate)Fe^{II}(CH$_3$CN)$_2$] (ClO$_4$)$_2$. The complexes show virtually the same electronic spectrum in the UV region, attributed to coordinated macrocycle, exhibiting fairly intense bands in the visible region at 559 and 602, and 527 and 596 nm for **4** and **5**, respectively (figure 2). These bands, considered too intense to be due to d–d transitions, are attributed to Fe(II)-to-macrocycle charge transfer having origin in the overlapping of the occupied metal d_{xz} and d_{yz} orbitals with vacant P_π* antibonding orbitals of the unsaturated segment of the macrocycle [14–16].

The electrochemical behaviors of both complexes were studied to provide more information on the nature of the complex in solution. Complex **5** is inactive from +1.5 to −1.5 V (potentials against the ferrocenium/ferrocene couple). Over the same potential range, **4** revealed only a one-electron reduction at −1.02 V and the corresponding oxidation occurs at −0.758 V *versus* Ag/Ag$^+$ reference electrode (see figure 3). This wave can be assigned to the [4]$^{0/+}$ species and is probably due to a redox process involving the macrocyclic ligand. Complex **4** that undergoes reduction is completely regenerated following electrochemical oxidation (the ratio of the peak currents $i$pa/$i$pc is ≈1.0), suggesting a chemically reversible [4]$^{0/+}$ one-electron

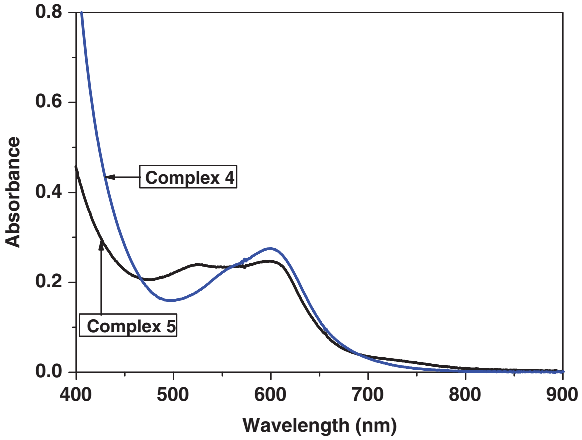


Figure 2. Visible absorption spectra of **4** and **5** in acetonitrile.

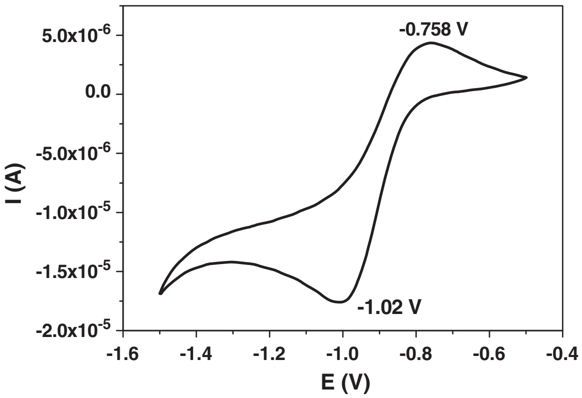


Figure 3. Cyclic voltammogram of [$Fe^{II}(pyN_3S_2)(ClO_4)_2$] performed on a Pt working electrode *vs.* a non-aqueous Ag/Ag^+ reference electrode; add 544 mV [300 mV, Ag/Ag^+ to SCE; +244 mV, SCE to SHE] to convert to standard hydrogen electrode (SHE); Fc/Fc^+couple in CH_3CN, $E_{1/2}$, 0.414 V (CV); supporting electrolyte 0.10 mol L^{-1} NBu_4PF_6, scan rate = 50 mVs^{-1}, complex concentration, 0.2×10^{-3} mol L^{-1}.

transfer process. However, the value of the limiting peak-to-peak separation (ΔE_p, 262 mV), which lies outside the normal values for a reversible one-electron redox process, suggests that the heterogeneous electron-transfer process in these complexes is not easily reversible [17] (ΔE_p, 60 mV for a reversible one-electron redox process) and may be accompanied by stereochemical reorganization [18].

3.1. *Molecular and crystal structure of 4*

Complex **4** is neutral and crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Crystallographic data and experimental details are

Table 2. Deviations (Å) of atoms from the least-squares planes through the macrocyclic MN_3S_2 unit.

	$[(pyN_3S_2)Fe(II)(ClO_4)_2]$ plane I	$[(pyN_3S_2)Fe(II)(ClO_4)_2]$ plane II	$[(pyN_3S_2)Zn(II)(ClO_4)_2]$ [19]
Metal	0.029(2)*	0.010(1)*	−0.02
N3(pyridino)	−0.067(2)*	−0.032(2)*	−0.05
N2(imino)	0.021(2)*	−0.442(2)*	0.57
N′1(imino)	0.045(2)*	0.499(2)*	−0.48
S1	−0.924(3)	−0.671(2)*	0.70
S2	0.997(3)	0.636(2)*	−0.73
C17	−0.046(3)*	0.022(4)	
C27	0.018(3)*	−0.242(5)	

*Atoms used to define the least-squares plane.

Table 3. Selected bond lengths (Å) and angles (°) for $[(pyN_3S_2)Fe^{II}(ClO_4)_2]$ (**4**).

Fe(1)–N(3)	2.092(3)	Fe(1)–S(1)	2.5998(9)
Fe(1)–N(2)	2.227(3)	Fe(1)–O(11)	2.322(2)
Fe(1)–N(1)	2.228(3)	Fe(1)–O(21)	2.290(3)
Fe(1)–S(2)	2.5521(9)		
N(3)–Fe(1)–N(2)	74.3(1)	O(21)–Fe(1)–O(11)	166.3(2)
N(3)–Fe(1)–N(1)	73.8(1)	N(2)–Fe(1)–S(1)	136.18(7)
N(2)–Fe(1)–N(1)	148.08(9)	N(3)–Fe(1)–S(1)	137.91(8)
N(3)–Fe(1)–O(21)	77.7(2)	N(1)–Fe(1)–S(1)	72.46(7)
N(2)–Fe(1)–O(21)	80.3(1)	N(3)–Fe(1)–S(2)	143.03(8)
N(1)–Fe(1)–O(21)	94.6(1)	N(2)–Fe(1)–S(2)	74.81(7)
N(3)–Fe(1)–O(11)	88.72(9)	N(1)–Fe(1)–S(2)	133.62(7)
N(2)–Fe(1)–O(11)	97.64(9)	O(11)–Fe(1)–S(2)	75.80(6)
N(1)–Fe(1)–O(11)	80.04(9)	O(21)–Fe(1)–S(2)	116.19(9)
O(21)–Fe(1)–S(1)	80.6(10)	O(11)–Fe(1)–S(1)	109.3(6)
S(2)–Fe(1)–S(1)	79.1(3)		

summarized in section 3 (table 1). Deviations from least-squares planes are given in table 2 and selected bond distances and angles are summarized in table 3. Single-crystal X-ray structure determination of **4** confirms the presence of the pentadentate [1 + 1] cyclic condensation ligand and shows that all potential donors of the ligand coordinate to iron(II) (see figure 4). Complex **4** has a seven-coordinate iron(II) centre with a distorted pentagonal-bipyramidal geometry, in which the nitrogen donors and the carbons of the ethylene bridge (C17, C27) of the macrocycle ligand reside in the equatorial plane (plane I, see table 2). The two sulfur donors deviate significantly from this plane by 0.924 Å (S1) and 0.997 Å (S2) sitting above and below the plane (see table 3). One oxygen donor each of the two perchlorates occupies the axial positions (O11, O21). To the best of our knowledge, this is the only seven-coordinate structure available for Fe(II) with the N_3S_2 pentadentate macrocycle. The conformation of the macrocycle in **4** may be compared with that of the zinc complex $[(pyN_3S_2)Zn^{II}(ClO_4)_2]$ containing the same N_3S_2 ligand reported previously [19]. Complex **4**, like $[(pyN_3S_2)Zn^{II}(ClO_4)_2]$, has a *C* distortion from the pentagonal-bipyramidal structure; the maximum deviation of an atom from the metal macrocycle plane (plane II, see table 2) is slightly smaller than in $[(pyN_3S_2)Zn^{II}(ClO_4)_2]$. The equatorial Fe–N distances [2.092(3) Å] for the unique Fe–N(3) bond and 2.227(3) and 2.228(3) Å for Fe–N(1) and

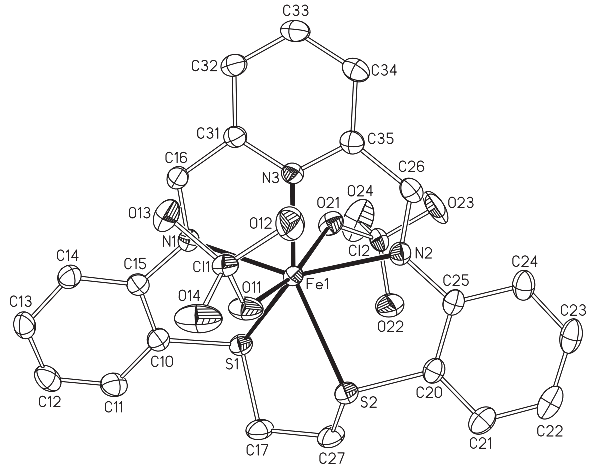


Figure 4. Thermal ellipsoid plot of the molecular structure of [(pyN$_3$S$_2$)Fe^{II}(ClO$_4$)$_2$] (**4**) showing the atom numbering scheme (50% probability level, hydrogen atoms, and disorder of the second perchlorate omitted for clarity).

Fe–N(2), respectively, are similar to those found for [(pyN$_3$S$_2$)Zn^{II}(ClO$_4$)$_2$], demonstrating that metal-N bonds in these complexes are not particularly sensitive to metal-ion size. As found for other pentagonal-bipyramidal complexes of macrocyclic ligands and particularly for iron(II) complexes, the metal-N(3) distance is the shortest [20, 21].

The conformation of the macrocycle in **4** may be compared with that reported recently for [(pyN$_3$S$_2$Me$_2$)Fe^{II}(ClO$_4$)$_2$], where pyN$_3$S$_2$Me$_2$ is a pentadentate open-chain ligand with the same set of donors [6]. Complex **4**, like [(pyN$_3$S$_2$Me$_2$)Fe^{II}(ClO$_4$)$_2$], has a seven-coordinate pentagonal-bipyramidal arrangement. Predictably, **4** is much more distorted with shorter bond distances, Fe–N (~2.18 Å) and Fe–S (~2.58 Å) compared to 2.30 Å and 2.69 Å for [(pyN$_3$S$_2$Me$_2$)Fe^{II}(ClO$_4$)$_2$]. These differences can be attributed to the formation of a macrocyclic chelate ring formed by linking the two phenyl rings with an ethylene bridge. The ethylene linkage in **4** induces steric strain leading to a relatively symmetrical displacement of the two sulfur donors above and below the equatorial plane of the pentagonal bipyramid. The absence of this ethylene linkage in the open chain chelate allows for a more planar geometry with longer bond distances. In the neutral **4**, the axial sites are occupied by coordinated perchlorates with bond distances Fe(1)–O(11) 2.322(2) Å and Fe(1)–O(21) 2.290(3) Å. The C1–O distances of the two coordinated oxygen atoms of 1.475(2) for Cl1–O11 and 1.458(4) Å for Cl2–O21 are longer than the C1–O distances of the uncoordinated oxygen atoms (~1.43 Å), which may suggest weakening of the C1–O bond through coordination of ClO$_4^-$ to Fe^{II}. Within the crystal packing, stacks of complex molecules along the crystallographic *c*-axis are formed (figure 5). Within these stacks neighboring molecules interdigitate slightly by their C21–C26 phenyl rings to form π–π interactions as indicated by a distance of 3.31 Å of two neighboring phenyl rings. This π-stacking arrangement leads to the formation of layers of complex molecules along the crystallographic *b*-axis.

By analogy with [(pyN$_3$S$_2$)Fe^{II}(ClO$_4$)$_2$] (**4**), known from a single-crystal X-ray study to contain a seven-coordinate structure, we suggest a similar structure for [(pyN$_3$Me$_2$S$_2$)

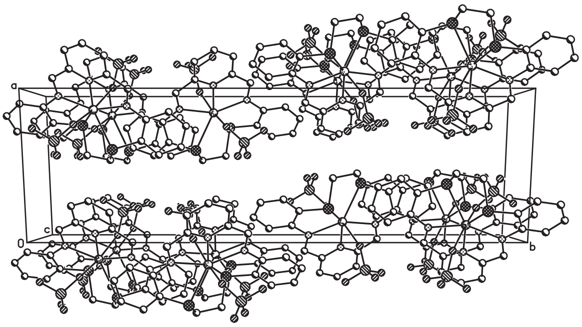


Figure 5. Crystal packing diagram of **4**, viewed along the crystallographic *c*-axis.

Fe^{II}(ClO$_4$)$_2$] (**5**), the two complexes differing only in the nature of the substituent at the imino-carbons. While small differences in the electronic spectra of both complexes were noted, they are not sufficiently clear either to support the above proposed structure or to detract from them.

4. Conclusion

The preparation and detailed characterization of high-spin seven-coordinate complexes **4** and **5** of the 15-membered N_3S_2 macrocyclic ligand are described. The coordination polyhedron is described as distorted pentagonal-bipyramidal with the macrocycle defining the pentagonal plane and the perchlorates occupying axial positions. The preference of the present structure to adopt a pentagonal bipyramid rather than a capped trigonal prism or a capped octahedron is presumably due to the ligand geometry rather than the crystal field stabilization energy that determines the coordination mode. Electrical conductivity measurements in acetonitrile show the displacement of the two perchlorate anions by acetonitrile. Work is now underway to investigate the reactivity for this type of complex to act as catalysts towards oxidation of different substrates.

Supplementary material

CCDC-852771 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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