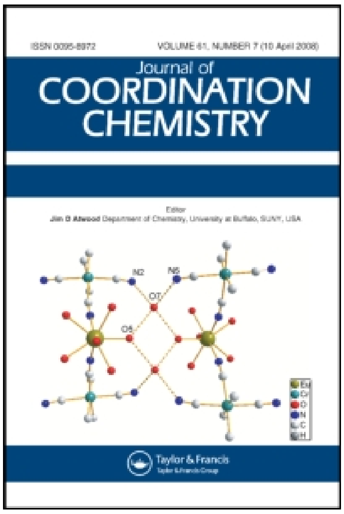

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Iron(III) complexes of tetradentate pyridylthioazophenol ligands: synthesis, spectroscopy, reactivity and structure

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Iron(III) complexes of tetradentate pyridylthioazophenol ligands: synthesis, spectroscopy, reactivity and structure

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A series of iron(III) complexes of novel tetradentate NSNO ligands (HL) has been prepared ($L = 2$-(2-pyridylmethylthio)-phenylazo-(p-substituted)-phenolates). Dark brown $[Fe(L)Cl_2]$ complexes have been characterized by elemental analyses, spectroscopic and other measurements. Magnetic moments at 25°C of the $[Fe(L)Cl_2]$ complexes are in the range 5.75–5.87 BM. Single-crystal X-ray structure analysis of one of the complexes, $[Fe(L1)Cl_2]$, revealed that the Fe(III) complexes are octahedral and monomeric, with the chlorides in the *cis* position. Electrochemical studies of $[Fe(L)Cl_2]$ in DMF give *quasi*-reversible voltammograms. Reactivities of $[Fe(L)Cl_2]$ complexes towards a variety of unidentate ligands ($X = CN^-$, N_3^-, pyridine, imidazole) indicate that the two chlorides are nonequivalent. Magnetic susceptibility data of the series of resulting iron(III) complexes, $[Fe(L)(X)Cl]^{n+}$ ($n = 0, 1$), are in accord with the Tanabe–Sugano theory.

Keywords: Iron(III); Pyridylthioazophenol ligands; Crystal structure; Reactivity

1. Introduction

The chemistry of N,S chelating ligands has been stimulated by the discovery of similar donor environments in several bioactive molecules [1–6]. Interest in the coordination chemistry of transition metal complexes involving N,S donors arises from applications in the fields of chemical and biological reactivity, and modeling of biomolecules. The coordination chemistry of iron(III) of nitrogen–sulfur donor sets, particularly those involving heterocyclic nitrogen, has generated considerable interest.

This article describes the chemistry of Fe(III) complexes of pyridylthioazophenolates, which are of interest because of the presence of hard donor azo-N and phenolato-O, borderline base pyridine-N and soft thioether-S donors. A novel series of Fe(III) complexes of tetradentate NSNO pyridylthioazophenols ligands is reported. One of the complexes, $[Fe(L1)Cl_2]$, has been subjected to single-crystal X-ray analysis to

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confirm structural details and the complex is found to be octahedral and monomeric, with the chlorides in the *cis* position (L1 = 2-(2-pyridylmethylthio)-phenylazo-4(-methyl)-phenolates). Reaction of the complexes with a variety of unidentate ligands ($X = CN^-$, N_3^-, pyridine, imidazole) produces mixed unidentate iron(III) complexes of the type $[Fe(L)(X)Cl]^{n+}$ ($n = 0$, 1) (L = 2-(2-pyridylmethylthio)-phenylazo-(p-substituted)-phenolates).

2. Experimental

All reagents were obtained from commercial sources and used without further purification. Tetra-*n*-butylammonium perchlorate was prepared by the addition of sodium perchlorate to a hot solution of tetra-*n*-butylammonium bromide (Aldrich). The product was recrystallized from aqueous ethanol and tested for the absence of bromide. Solvents were distilled from an appropriate drying agent [7].

2.1. *Physical measurements*

IR spectra (KBr disks) were recorded using a Jasco 420 FTIR spectrophotometer and electronic spectra with a Jasco V-570 spectrophotometer. Microanalyses were performed with a Perkin Elmer 2400 CHN instrument; iron analysis was by AAS [8]. Molar conductances (Λ_M) were measured using a Systronics 304 conductivity meter, with ca 10^{-3} M solutions in MeOH. Magnetic moments (μ, BM) were measured with a PAR 155 vibrating sample magnetometer. Electrochemical measurements were carried out using a computer-controlled EG&G PAR 270 VERSTAT electrochemical instrument with Ag/AgCl, Pt-disk working and Pt-wire auxiliary electrodes. All measurements were made at 298 K in dry dimethylformamide with $[Bu_4N]ClO_4$ as supporting electrolyte. Experimental solutions were deoxygenated by bubbling with research grade dinitrogen. Reported potentials are uncorrected for junction potential.

2.2. *Syntheses*

2.2.1. Preparation of the ligands (HL). Ligands (HL) were prepared by coupling different *para*-substituted phenols with diazotized 2-(2-pyridylmethylthio)aniline, following a literature procedure [9].

2.2.2. Preparation of [Fe(L)Cl$_2$] complexes. Preparation of the Fe(III) complexes followed a common procedure. To a methanolic solution (15 cm^3) of L (1.0 mmol), ferric chloride hexahydrate (1.0 mmol) solution was added dropwise and the resulting solution stirred for 1 h. The solution was dried at ambient temperatures. The product was collected by washing with cold MeOH/H_2O and recrystallized from dichloromethane (yield 80–85%).

2.2.3. [Fe(L)(X)Cl] ($X = CN^-$, N_3). To a solution of $[Fe(L)Cl_2]$ complex in MeOH was added a solution of sodium azide (NaN_3) or sodium cyanide (NaCN) in the minimum amount of water in an equimolar ratio. The mixture was warmed at 45–50°C on a water bath for 10–15 min and then filtered. The filtrate was kept overnight and the resulting precipitate collected, washed with MeOH, water and ether, and dried *in vacuo*.

2.2.4. [Fe(L)(X)Cl]PF$_6$ (X = Him, py). To a solution of [Fe(L)Cl$_2$] in methanol was added an excess amount of imidazole (im) or pyridine (py). The mixture was warmed at 60–65°C on a water bath for 25–30 min and then filtered. To the filtrate was added a solution of ammonium hexafluorophosphate, the mixture was stirred for 30 min and then placed in a refrigerator for several days. The product was collected by filtration, washed with MeOH and ether and dried *in vacuo*.

2.3. *X-ray crystal structure*

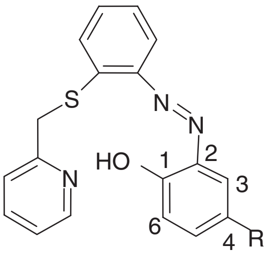
Single crystals of [Fe(L1)Cl$_2$] (**2a**) suitable for X-ray analysis were grown by slow evaporation of a methanol : toluene (1 : 2) solution of the complex at 298 K. A suitable crystal was mounted on a Bruker SMART CCD diffractometer equipped with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by the Patterson method, followed by successive Fourier syntheses. Full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 with anisotropic displacement parameters for all nonhydrogen atoms. Hydrogen atoms were constrained to ride on their respective carbon atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the parent atom. Refinement converged to $R = 0.0265$, $wR2 = 0.0630$ [$I > 2\sigma(I)$]. Neutral atom scattering factors [10a] were used throughout. All calculations were carried out using SHELXS-97 [10b], SHELXL-97 [10c], PLATON 99 [10d] and ORTEP3 [10e] programs. A summary of the crystallographic data is given in table 1.

3. Results and discussion

The series of 2-(2-pyridylmethylthio)-phenylazo-(4-methyl)phenolates (figure 1) was prepared. They act as tetradentate monobasic NSNO chelating ligands. Fe(III) complexes

Table 1. Crystallographic data for complex **2a**.

Empirical formula	$C_{19}H_{16}Cl_2FeN_3OS$
Formula weight	461.16
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1$
Unit cell dimensions	$a = 8.9145(8)$ Å $b = 10.4522(9)$ Å $c = 10.9038(10)$ Å $\beta = 102.222(2)°$
Volume	992.95(15) Å^3
Z, Calculated density	2, 1.542 Mg m^{-3}
Absorption coefficient	1.148 mm^{-1}
F(000)	470
θ range for data collection	1.95 to 28.28
Reflections collected/unique	6151/4164 [R(int) = 0.0166]
Completeness to $\theta = 28.28°$	95.8%
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.956
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0265$, $wR2 = 0.0630$
R indices (all data)	$R1 = 0.0302$, $wR2 = 0.0642$
Absolute structure parameter	−0.017(11)
Largest diff. peak and hole	0.259 and −0.165 e Å^{-3}



HL

R = Me	^{t}Bu	Cl	NO_2	3,4-Benzo
HL = 1	2	3	4	5

Figure 1. Structures of the ligands.

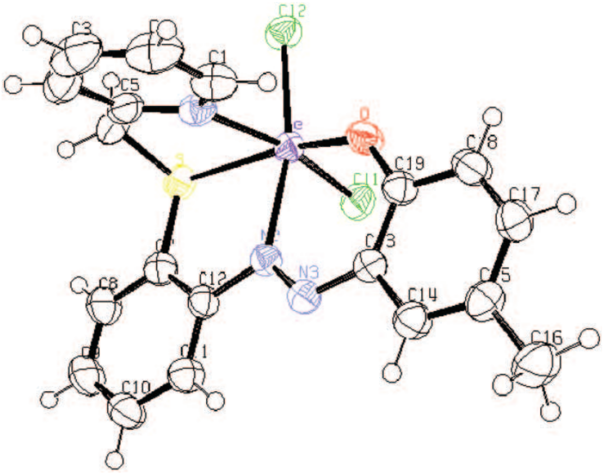


Figure 2. An ORTEP view of the complex [Fe(L1)Cl_2] with thermal ellipsoids drawn at the 50% probability level, showing the atom numbering scheme.

of the ligands are soluble in common organic solvents. Conductivity measurements of [Fe(L)Cl_2] in methanol suggest that they exist as nonelectrolytes in solution.

3.1. *Structure of [Fe(L1)Cl_2] (2a)*

An ORTEP view of **2a** is shown in figure 2 with the atom numbering scheme. Selected bond distances and angles are listed in table 2. In the monomeric complex, iron is bonded to the pyridylthioazophenolate ligand (L1) and two chloride ions. The coordination geometry is distorted octahedral with ozo-N, phenolate-O, thioether-S atoms and one chloride ion occupying the basal plane; the pyridine-N atom and another chloride ion lie in axial sites. The axial Fe–pyridine-N(1) bond distance [2.219(2) Å] is the same as the equatorial Fe–azo-N(2) distance [2.220(2) Å]. Here, both are notably longer than typical Fe(III)–N(pyridine) in complexes of pyridine [11], because of the weak donor capacity of thioether-S, which is involved in the formation of two adjacent five-membered chelate rings. The thioether Fe–S bond distance of 2.505(1) Å is longer

Table 2. Selected bond lengths [Å] and angles [°] for complex **2a**.

Fe–O	1.879(2)	S–C(7)	1.778(3)
Fe–N(1)	2.219(2)	S–C(6)	1.805(3)
Fe–N(2)	2.220(2)	O–C(19)	1.305(3)
Fe–Cl(2)	2.293(1)	N(1)–C(5)	1.338(4)
Fe–Cl(1)	2.304(1)	N(1)–C(1)	1.345(3)
Fe–S	2.505(1)	N(2)–N(3)	1.258(3)
N(3)–C(13)	1.379(3)	N(2)–C(12)	1.448(3)
C(15)–C(16)	1.520(4)	C(15)–C(17)	1.405(4)
O–Fe–N(1)	91.95(9)	O–Fe–N(2)	85.49(7)
N(1)–Fe–N(2)	82.88(8)	O–Fe–Cl(2)	102.87(5)
N(1)–Fe–Cl(2)	86.30(5)	N(2)–Fe–Cl(2)	166.57(6)
O–Fe–Cl(1)	97.38(7)	N(1)–Fe–Cl(1)	167.25(6)
N(2)–Fe–Cl(1)	89.19(6)	Cl(2)–Fe–Cl(1)	99.98(3)
O–Fe–S	163.30(6)	N(1)–Fe–S	79.04(6)
N(2)–Fe–S	79.51(6)	Cl(2)–Fe–S	90.65(3)
Cl(1)–Fe–S	89.74(3)	C(7)–S–Fe	99.86(9)
C(7)–S–C(6)	101.48(13)	C(6)–S–Fe	97.83(10)
C(19)–O–Fe	133.33(15)	C(5)–N(1)–Fe	121.86(18)
N(3)–N(2)–Fe	127.05(16)	C(12)–N(2)–Fe	120.54(17)
C(1)–N(1)–Fe	119.3(2)	N(3)–N(2)–C(12)	112.38(19)
N(2)–N(3)–C(13)	122.4(2)	N(1)–C(1)–C(2)	121.9(3)

than Fe(III)–sulfinato-S [12] because of the weaker bond formation with the thioether sulfur compared with the sulfinato group to Fe(III). Here this bond is associated with the strong *trans* Fe–O bond [1.879(2) Å]. However, the Fe–S bond distance is somewhat shorter than in examples reported previously [13]. The equatorial Fe–Cl(2) bond distance [2.293(1) Å] is almost equal to the axial Fe–Cl(1) distance [2.304(1) Å]. However, both the Fe–Cl bonds are within the range of previously reported Fe–Cl bond distances [14].

3.2. *Spectroscopic properties*

The ligands exhibit medium-intensity IR bands at ca $3300\,\mathrm{cm}^{-1}$ (O–H of H-bonded phenolic OH) [15], which are absent in all of the complexes, indicating coordination of oxygen to the metal center [16]. The $\nu_{\mathrm{N=N}}$ mode of the free ligand (1495–$1505\,\mathrm{cm}^{-1}$) is shifted to lower wavenumbers ($\Delta \approx 20$–$30\,\mathrm{cm}^{-1}$) in the complexes, suggesting coordination of the metal ions to the azo group [17]. The $\nu_{\mathrm{N=N}}$ band is observed at 1465–$1478\,\mathrm{cm}^{-1}$ for all of the complexes. In addition, $\nu_{\mathrm{C{-}S}}$, at $790\,\mathrm{cm}^{-1}$ for the ligands, shifts to $760\,\mathrm{cm}^{-1}$ for the complexes. Magnetic susceptibility data (table 3) reveal spin-only values for all complexes.

Electronic absorption spectra of $[\mathrm{Fe(L)Cl_2}]$ complexes were recorded at room temperature in MeOH (table 4). Spectra of the free ligands and the complexes exhibit absorptions below 400 nm corresponding to intramolecular $\pi \rightarrow \pi^*$ and $\mathrm{n} \rightarrow \pi^*$ transitions [18]. A band in the range 488–510 nm in the complexes is attributed to an intra-ligand transition whereas a broad, weak band ($\varepsilon = 558$–$749\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) at 615–629 nm in the complexes is assigned to d(Fe) $\rightarrow \pi^*$ (ligand) charge transfer transitions [19].

3.3. *Electrochemistry*

Redox properties of complexes **2a–e** were examined by cyclic voltammetry (table 4) referenced to Ag/AgCl. In solution all compounds displayed a *quasi*-reversible

Table 3. Microanalytical data for the Fe(III) complexes.

	Found (Calcd)					
Compound	C	H	N	Fe	μ/BM	Λ*
[Fe(L1)Cl$_2$], **2a**	49.55	3.59	9.01	12.21		
	(49.47)	(3.47)	(9.11)	(12.11)	5.79	15
[Fe(L2)Cl$_2$], **2b**	52.28	4.45	8.47	10.98		
	(52.50)	(4.37)	(8.35)	(11.11)	5.75	11
[Fe(L3)Cl$_2$], **2c**	45.01	2.83	8.61	11.67		
	(44.87)	(2.7)	(8.72)	(11.60)	5.79	13
[Fe(L4)Cl$_2$], **2d**	43.76	2.71	11.21	11.90		
	(43.91)	(2.64)	(11.38)	(11.35)	5.87	16
[Fe(L5)Cl$_2$], **2e**	52.98	3.27	8.56	11.39		
	(53.13)	(3.22)	(8.45)	(11.24)	5.81	10
[Fe(L1)(CN)Cl], **3a**	53.28	3.61	12.24	12.18		
	(53.17)	(3.54)	(12.41)	(12.37)	3.95	13
[Fe(L2)(CN)Cl], **3b**	56.08	4.39	11.28	11.39		
	(55.94)	(4.46)	(11.35)	(11.32)	3.94	11
[Fe(L3)(CN)Cl], **3c**	48.25	2.69	11.95	12.02		
	(48.32)	(2.75)	(11.87)	(11.84)	4.10	10
[Fe(L4)(CN)Cl], **3d**	47.11	2.59	14.62	11.31		
	(47.27)	(2.69)	(14.51)	(11.58)	3.94	12
[Fe(L5)(CN)Cl], **3e**	56.76	3.33	11.35	11.90		
	(56.63)	(3.28)	(11.49)	(11.46)	3.93	9
[Fe(L1)(N$_3$)Cl], **4a**	48.52	3.46	17.99	11.69		
	(48.78)	(3.42)	(17.97)	(11.95)	5.87	10
[Fe(L2)(N$_3$)Cl], **4b**	52.01	4.39	16.35	10.81		
	(51.83)	(4.32)	(16.49)	(10.96)	5.95	12
[Fe(L3)(N$_3$)Cl], **4c**	44.54	2.71	17.09	11.79		
	(44.27)	(2.66)	(17.22)	(11.45)	5.88	10
[Fe(L4)(N$_3$)Cl], **4d**	42.28	2.50	19.77	10.99		
	(42.34)	(2.61)	(19.66)	(11.21)	5.87	11
[Fe(L5)(N$_3$)Cl], **4e**	52.58	3.14	16.58	11.29		
	(52.45)	(3.18)	(16.69)	(11.09)	5.84	12
[Fe(L1)(Him)Cl]PF$_6$, **5a**	41.28	3.17	10.89	8.81		
	(41.35)	(3.13)	(10.96)	(8.75)	5.92	102
[Fe(L2)(Him)Cl]PF$_6$, **5b**	44.89	3.91	10.42	8.37		
	(44.95)	(3.82)	(10.29)	(8.21)	5.94	100
[Fe(L3)(Him)Cl]PF$_6$, **5c**	38.14	2.67	10.73	8.51		
	(38.25)	(2.58)	(10.62)	(8.48)	5.92	99
[Fe(L4)(Him)Cl]PF$_6$, **5d**	37.74	2.63	12.31	8.57		
	(37.65)	(2.54)	(12.55)	(8.34)	5.90	104
[Fe(L5)(Him)Cl]PF$_6$, **5e**	44.58	2.89	10.27	8.18		
	(44.49)	(2.96)	(10.38)	(8.28)	5.88	89
[Fe(L1)(py)Cl]PF$_6$, **6a**	44.01	3.29	8.49	8.79		
	(44.35)	(3.23)	(8.62)	(8.60)	4.31	98
[Fe(L2)(py)Cl]PF$_6$, **6b**	46.89	4.01	7.92	7.97		
	(46.86)	(3.90)	(8.10)	(8.08)	4.23	89
[Fe(L3)(py)Cl]PF$_6$, **6c**	41.14	2.77	8.47	8.50		
	(41.20)	(2.69)	(8.36)	(8.34)	4.28	93
[Fe(L4)(py)Cl]PF$_6$, **6d**	40.71	2.73	10.31	8.67		
	(40.57)	(2.64)	(10.29)	(8.21)	4.29	99
[Fe(L5)(py)Cl]PF$_6$, **6e**	47.48	3.20	8.37	8.18		
	(47.27)	(3.06)	(8.17)	(8.15)	4.21	83

*mho cm^2 mol^{-1}.
SI units: s · cm^2 · mol^{-1}.

Table 4. Electronic absorption and cyclic voltammetry data for the [Fe(L)Cl$_2$] complexes.

Compound	λ/nm (ε/M^{-1}cm^{-1})	$E^{\circ\prime}$/mV (ΔE_p/mV)	[E_{pa}/mV, E_{pc}/mV]
2a	490 (2700), 622 (728)	146.5 (287)	[290, +0.3]
2b	488 (2695), 629 (558)	136.5 (281)	[277, −0.4]
2c	502 (2822), 620 (749)	142.5 (277)	[281, +0.4]
2d	510 (2205), 615 (565)	116.8 (250.4)	[242, −8.4]
2e	504 (2954), 619 (612)	118 (270)	[253, −17]

voltammogram with $i_{pc}/i_{pa} \approx 1$. ΔE_p is high in comparison to general observations, probably because of the stability of the corresponding Fe(II) species. Incorporation of a thioether donor in the ligands stabilizes the lower oxidation state of iron in DMF [13a]. The influence of substituents on the ligands is apparent from the data.

3.4. *Reactivity of the [Fe(L)Cl$_2$] complexes*

The [Fe(L)Cl$_2$] complexes react with sodium azide or sodium cyanide in MeOH–H$_2$O at 45–50°C to produce [Fe(L)(X)Cl] (X = CN$^-$, N$_3$), whereas [Fe(L)(X)Cl]PF$_6$ (X = Him, py) complexes were obtained by reacting the appropriate base with [Fe(L)Cl$_2$] at 60–65°C and adding hexafluorophosphate. Probably only the axial chloro ligand is replaced. All the derivatives of general formula [Fe(L)(X)Cl]$^{n+}$ ($n = 0$, 1) have been isolated and characterized by IR and elemental analyses (table 3). Cyano and azido derivatives display absorption bands around 2130 and 2065 cm^{-1}, respectively, due to $\nu_{C\equiv N}$ and $\nu_{asym(NNN)}$, respectively, whereas imidazole and pyridine derivatives of [Fe(L)Cl$_2$] display absorption bands around 840 and 540 cm^{-1} due to $\nu_{(PF6^-)}$. Conductivity measurements of complexes **3** and **4** in methanol solution indicate that they are nonelectrolytes and **5** and **6** are 1 : 1 electrolytes. Magnetic susceptibility data (table 3) are in accord with the Tanabe–Sugano theory with the ligands varying over a broad range of the spectrochemical series.

Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 254717 for compound **2a**. Copies of this information are available on request free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.ac.uk or http://www.ccdc.cam.ac.uk).

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