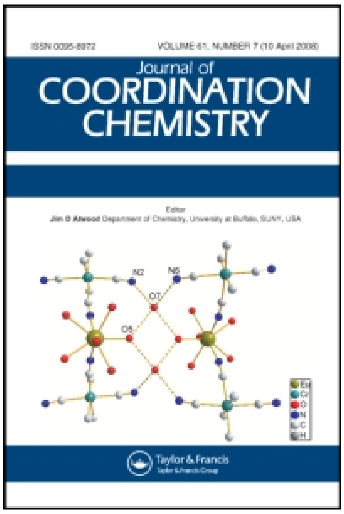

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SYNTHESIS AND CHARACTERIZATION OF THE NOVEL BRIDGED LIGAND 5,8-DIMETHYL-1,5,8,12-TETRAAZABICYCLO[10.3.2]HEPTADECANE AND ITS COMPLEXES WITH IRON(II) AND MANAGANESE(II) IONS

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SYNTHESIS AND CHARACTERIZATION OF THE NOVEL BRIDGED LIGAND 5,8-DIMETHYL-1,5,8,12-TETRAAZABICYCLO[10.3.2]HEPTADECANE AND ITS COMPLEXES WITH IRON(II) AND MANGANESE(II) IONS

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The bridged tetradentate ligand 5,8-dimethyl-1,5,8,12-tetraazabicyclo[10.3.2]heptadecane (L_1) has been prepared, and its complexes with manganese(II) and iron(II) synthesized and characterized. The crystal structure of MnL_1(NCS)$_2$ has been determined; the Mn is octahedral with *cis*-NCS ligands, and the asymmetric unit contains two independent molecules differing slightly in the Mn—N—C angles. The oxidation of the complexes by hydrogen peroxide is also discussed.

Keywords: Macrobicyclic ligand; Bridged macrocycle; Manganese complexes; Iron complexes

INTRODUCTION

The synthesis of intramolecularly bridged saturated aza-macrocyclic ligands is currently of great interest [1,2]. The resulting topologically constrained ligand frameworks are expected to provide complexes of increased stability with respect to ligand dissociation, providing there is appropriate complementarity between the ligand and the metal ion [3]. In these ligands,

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different modes of bridging are possible, many of them involving the bridging of either adjacent [1] or nonadjacent (*cross-bridged*) nitrogen atoms [2]. Weisman *et al.*, have previously reported the elegant synthesis of a series of 12-, 13-, and 14 -membered cross-bridged macrocycles [2a, c]. In the work reported here, we have examined the application of that particular bridging reaction to the larger 15-membered macrocycle, 1,4,8,12-tetraazacyclopentadecane. Surprisingly a similar preparative route to that of Weisman leads to the *adjacent* bridged macrocycle 5,8-dimethyl-1,5,8,12-tetraazabicyclo[10.3.2]heptadecane (L_1). The coordination chemistry of this ligand with iron(II) and manganese(II) ions has been investigated, and the oxidation chemistry of the resulting complexes examined.

RESULTS AND DISCUSSION

Ligand Synthesis

The synthetic process is outlined in Figure 1. The bridging reaction between glyoxal and 1,4,8,12-tetraazacyclopentadecane proceeded as reported for the smaller macrocycles by Weisman *et al.* [4] Dialkylation with methyl iodide, however, yielded a dark brown hygroscopic solid in contrast to the pure white compounds reported by Weisman for the smaller macrocyclic ring systems. From a mass spectrum, it appears that the brown compound contains the desired dialkylated product (peak [for $C_{15}H_{30}N_4I_1]^+$ at $m/z = 393$), but attempted purification of this material by a variety of

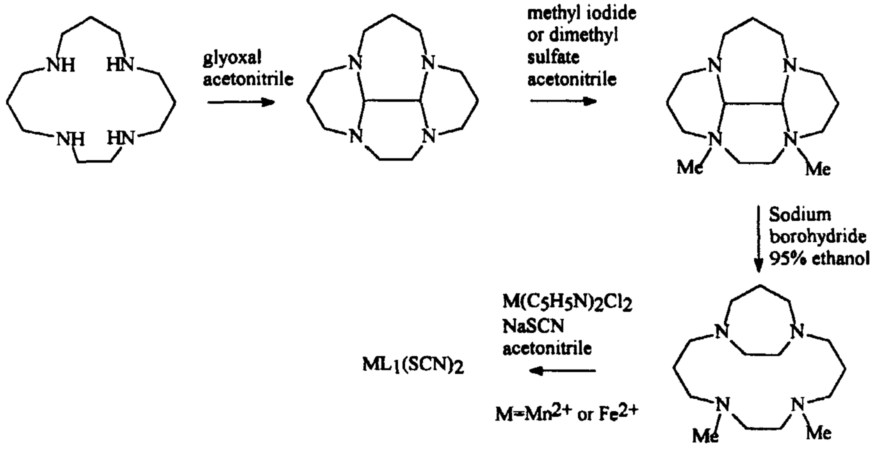

FIGURE 1 Synthesis and metal complexation reaction for the ligand L_1.

techniques proved unsuccessful, mainly due to its hygroscopic nature. Attempts at isolation of the reaction product after only 24 hours, rather than 3 days, yielded a compound exhibiting a mass spectrum corresponding to only the monoalkylated species. Two other alkylating agents were investigated in this reaction, namely methyl-*p*-toluene sulfonate and dimethyl sulfate. In the former case the product seemed to correspond to the monoalkylated product; with the latter, the desired dialkylated product was obtained.

Without further purification, this dialkylated product was reduced with sodium borohydride to yield the macrobicyclic ligand L_1 [2a, c]. Surprisingly, the ^{13}C NMR of the product from this reaction displayed predominantly an eight peak spectrum. This corresponds to the structure L_1 rather than the expected *cross-bridged* derivative. The latter compound would have produced a more complicated spectrum because of its lower symmetry. With regard to formation of the smaller ring systems, Weisman notes that the conformation of the intermediate bisaminal is the determining factor in the alkylation process. From this perspective it would appear that the larger ring system adopts a significantly different conformation, favoring a different alkylation pattern. The same product was obtained with either methyl iodide or dimethyl sulfate as alkylating agent.

The ligand L_1 is expected to be less rigid than the corresponding *cross-bridged* macrocycle, although the adjacent bridge is also expected to increase the rigidity of the chelating system. Since ligand L_1 is homoleptic with four tertiary amine donors it is expected to exert a relatively strong ligand field [3b] and to be reasonably resistant to ligand oxidation when bound to metal ions, properties that merit further investigation [5].

Reaction of L_1 with Manganese(II) Ions

Initially the ligand was combined under anhydrous conditions with bis(pyridine)manganese(II) chloride, yielding a white powder. Complex formation was confirmed from the mass spectrum of the product by the appearance of a peak for $[Mn_1C_{15}H_{32}N_4]^+$ at $m/z = 358$; however, a consistent elemental analysis could not be obtained and methanol solutions of the complex gradually discolored upon exposure to the air, eventually precipitating a black powder. In addition to the peak identified with the complex, the mass spectrum of this solution shows a new peak corresponding to a protonated ligand species. This suggests that ligand dissociation has occurred, a problem previously found by Bryan *et al.*, with the ligand meso-5,5,7-12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane [6].

The complexation reaction was therefore repeated using a salt of the stronger field thiocyanate ligand and from this reaction, the pure complex $MnL_1(NCS)_2$ was obtained. The complex was characterized by spectroscopic and analytical measurements, and by crystal structure determination (Fig. 2; Tab. I). The asymmetric unit in the crystal contains two independent molecules differing only in the positioning of the *cis*-bound thiocyanates, with one significant variation between the Mn—N—C angles (Fig. 3). The manganese(II) ions have *pseudo* octahedral geometry, with the macrobicyclic ligand adopting a folded conformation. The Mn—N(macrocycle) distances are typical of those for manganese(II), although the substantial lengthening (0.2–0.3 Å compared to the remaining Mn—N distances) of the Mn—N(113)/N(213) distance compared to the other dimensions is

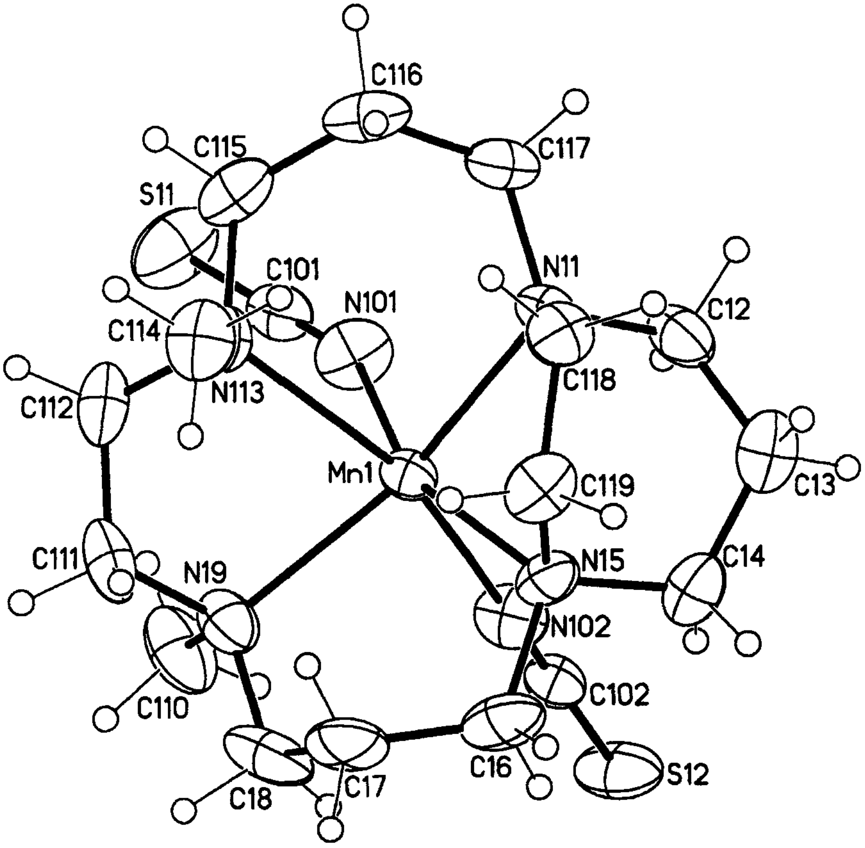

FIGURE 2 X-ray crystal structure of $MnL_1(SCN)_2$: one of the two non-identical molecules is shown.

TABLE I Selected bond lengths [Å] and angles [deg]

	Molecule 1	*Molecule* 2
Mn(1)—N(101)	2.138(6)	2.148(5)
Mn(1)—N(102)	2.220(5)	2.210(5)
Mn(1)—N(11)	2.278(4)	2.288(6)
Mn(1)—N(15)	2.276(5)	2.314(6)
Mn(1)—N(19)	2.253(5)	2.286(6)
Mn(1)—N(113)	2.558(4)	2.497(5)
N(101)—C(101)	1.150(7)	1.167(7)
N(102)—C(102)	1.153(7)	1.157(7)
C(101)—S(11)	1.629(8)	1.624(6)
C(102)—S(12)	1.632(6)	1.636(6)
N(101)—Mn(1)—N(102)	85.9(2)	85.7(2)
N(101)—Mn(1)—N(11)	95.4(2)	95.5(2)
N(102)—Mn(1)—N(11)	115.9(2)	115.8(2)
N(101)—Mn(1)—N(15)	158.1(2)	157.7(2)
N(102)—Mn(1)—N(15)	84.3(2)	84.9(2)
N(101)—Mn(1)—N(19)	100.4(2)	103.0(2)
N(102)—Mn(1)—N(19)	88.6(2)	88.7(2)
N(11)—Mn(1)—N(15)	71.6(2)	70.8(2)
N(11)—Mn(1)—N(19)	151.8(2)	150.4(2)
N(15)—Mn(1)—N(19)	98.9(2)	96.9(2)
N(101)—Mn(1)—N(113)	87.8(2)	88.8(2)
N(102)—Mn(1)—N(113)	162.8(2)	162.6(2)
N(11)—Mn(1)—N(113)	80.6(2)	81.2(2)
N(15)—Mn(1)—N(113)	106.7(2)	105.7(2)
N(19)—Mn(1)—N(113)	76.9(2)	76.5(2)
C(101)—N(101)—Mn(1)	155.3(6)	156.0(5)
N(101)—C(101)—S(11)	178.5(5)	178.6(6)
C(102)—N(102)—Mn(1)	171.3(5)	151.5(5)
N(102)—C(102)—S(12)	178.9(6)	177.1(6)

noteworthy and without obvious explanation. These are the only ligand N-atoms *trans* to another such atom, but if the lengthening is due to a *trans*-effect, it is surprising that the Mn—N(11)/N(21) distances are not also lengthened.

The IR spectrum of the complex shows only a single set of peaks for the thiocyanates, suggesting similar binding strengths between the different positions and only minimal coupling between them; the peaks at 2062 and 773 cm^{-1} are consistent with nitrogen-bound thiocyanate [7]. The conductivity of the complex in acetonitrile (87 $\omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$) is low for a uni-univalent electrolyte, suggesting incomplete dissociation of a single anion. Acetonitrile solutions of the manganese(II) complex appear to be stable upon exposure to the air. The magnetic susceptibility was determined to be 5.23 m_B, approaching that for a high spin octahedral d^5 complex. The ESR spectrum as a frozen glass in an acetonitrile/methanol mixture displays a six line spectrum, arising from the nuclear hyperfine interaction with the manganese nucleus (1 = 5/2) (Fig. 4).

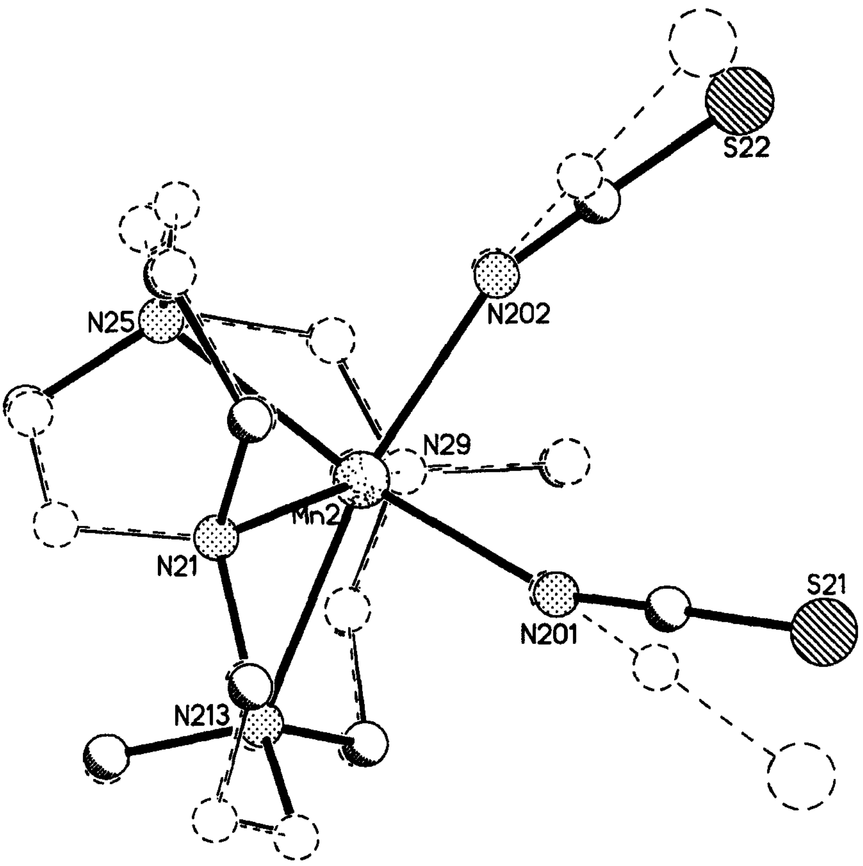

FIGURE 3 X-ray crystal structure of MnL_1(SCN)$_2$ with the two independent molecules in the asymmetric unit superimposed.

Reaction with Iron(II) Ions

As with manganese(II), reaction between the ligand and the metal ion source, Fe(py)$_2$Cl$_2$ in this case, resulted in an impure product. Consequently the thiocyanate complex FeL_1(NCS)$_2$ was synthesized and shown by elemental analysis to be the analytically pure monohydrate. The IR spectrum again shows one set of peaks for nitrogen bound thiocyanate (2061 cm^{-1} and 802 cm^{-1}) [7]. The results of conductivity measurements in acetonitrile (134 ω^{-1}cm^{2}mol^{-1}) indicate that the complex is a 1 : 1 electrolyte. In contrast to the manganese complex, acetonitrile solutions of the iron complex change with time upon exposure to air, slowly becoming yellow. On prolonged exposure a yellow powder is deposited.

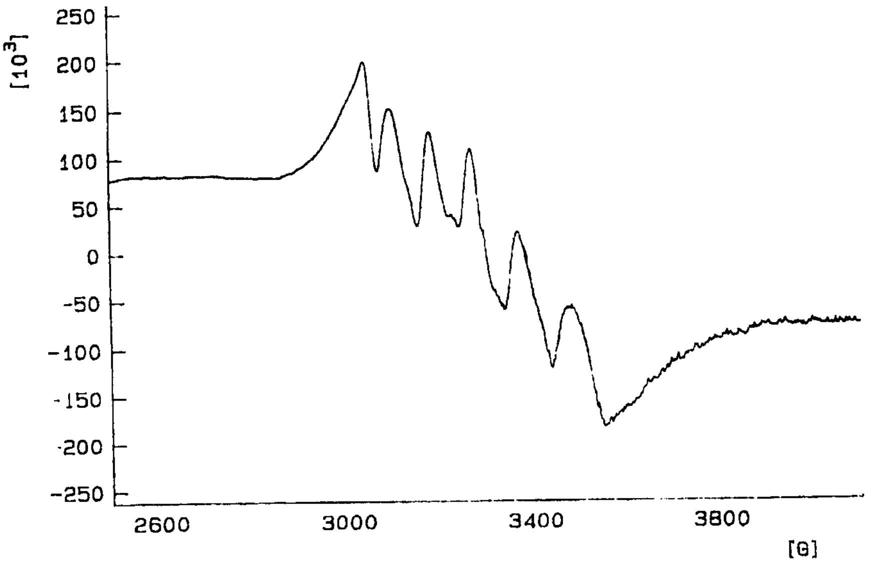

FIGURE 4 ESR of $MnL_1(SCN)_2$ in methanol/acetonitrile at 77 K.

The ^1H NMR spectrum of the iron(II) complex (under nitrogen in deutero-acetonitrile) is rather broad in nature suggesting paramagnetism. Dissolution in deutero-pyridine causes an immediate color change to bright yellow/green and the ^1H NMR spectrum becomes sharp. Clearly the complex becomes low spin and diamagnetic in pyridine solution. Earlier work involving the bis(thiocyanato)iron(II) complexes of 1,4,8,11-tetraazacyclotetradecane and 1,4,8,12-tetraazacyclopentadecane raises the possibility of a spin equilibrium since both the bis(thiocyanato) and the bis(acetonitrile) derivatives of the former were found to be low spin and those of the latter, high spin [8], but the bis(thiocyanato)(1,4,8,11-tetraazacyclotetradecane) complex dissociates an anionic ligand and becomes high spin in some solutions [9].

A mass spectrum of green crystals grown from an acetonitrile solution containing pyridine, exhibited only a peak [for $Fe_1C_{16}H_{32}N_5S_1]^+ = [Fe(L_1)NCS]^+$ at $m/z = 382$. This shows that any pyridine molecules associated with the color change are lost under the conditions of the mass spectral experiment.

Cyclic voltammetric data for the two new complexes are summarized in Table II. The manganese complex undergoes an irreversible oxidation reaction at $E_{1/2} = 0.85$ V *vs.* SHE, with $E_a - E_c = \delta E = 325$ mV and a completely irreversible reduction at $E_c = 0.21$ V *vs.* SHE. The poor reversibilities

TABLE II Cyclic Voltammetry (in acetonitrile, volts *vs.* SHE)

$MnL_1(SCN)_2$[a]	$MnL_1(SCN)_2$[b]	$FeL_1(SCN)_2$[a]	$FeL_1(SCN)_2$[c]
$E_c = 0.21$	$E_c = 0.16$	$E^1_{1/2} = 0.47$ $\delta E = 0.09$	$E^1_{1/2} = 0.39$ $\delta E = 0.115$
$E^2_{1/2} = 0.85$ $\delta E = 0.325$	$E^2_{1/2} = 0.88$ $\delta E = 0.125$	$E_a = 0.72$	$E_a = 0.62$

[a] performed under argon.
[b] after addition of hydrogen peroxide.
[c] in air.

of these processes indicate a lack of stability of the oxidized and reduced complexes, a situation mentioned above. The iron complex is somewhat more stable, perhaps because the tetradentate ligand can better accommodate the iron ion in its trivalent oxidation state [10]. The iron(III/II) couple gives a *quasi*-reversible wave at 0.47 V *vs.* SHE with $\delta E = 90\,\text{mV}$. A second irreversible oxidation process indicates a still higher state for the iron. Oxidation of either metal complex in solution with hydrogen peroxide or oxygen results in decreased values for the half wave potentials, probably because of changes in the monodentate ligands.

Oxidation with Hydrogen Peroxide

The oxidation of macrocyclic manganese(II) complexes with hydrogen peroxide commonly leads to higher oxidation states, often involving oxo-bridged species [11]. Addition of hydrogen peroxide to acetonitrile solutions of both the manganese and iron complexes of L_1 causes visible indications of reaction at the metal centers. The solution containing the iron complex darkens to a purple color, oxygen is evolved and an orange precipitate forms. Purple colors of solutions containing hydrogen peroxide and iron complexes have been assigned to a charge-transfer transition [12] between iron(III) and a monodentate peroxide ion.

The oxidized species formed from the manganese(II) complex is more robust and the UV spectrum of its solution was easily recorded. This transformation appears to be complete in approximately 20 minutes. The spectrum shows two new peaks at 280 and 424 nm. Bands at approximately 280 nm have been reported for a series of oxo-bridged manganese(IV) dimers, suggesting oxo-bridge formation with our complex also [11]. After approximately 60 minutes a precipitate appears, indicating decomposition.

Attempts were made to identify the oxidized species in both complex systems by adding hydrogen peroxide to acetonitrile solutions of the complexes and then recording FAB$^+$ mass spectra. In both cases the

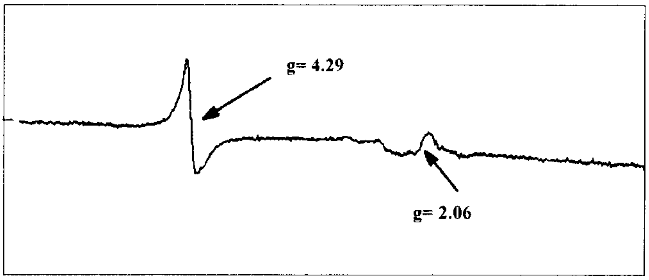

FIGURE 5 ESR of $FeL_1(SCN)_2 + H_2O_2$ in acetone at 77 K.

spectrum only showed peaks corresponding to starting materials. The oxidized species were also investigated by ESR spectroscopy. No signals were observed for the oxidized manganese solution when the spectrum was recorded on a frozen acetonitrile/methanol glass. When the purple solution of the iron complex was frozen immediately after coloration, the ESR spectrum displayed signals at $g = 4.29$ and at $g = 2.06$ (broad) (Fig. 5). Recent publications on related iron systems assign values of $g = 4.30$ to rhombic six-coordinate high spin iron(III) complexes, while the values around $g = 2$ are assigned to low spin six-coordinate rhombic peroxo iron(III) species [12, 13]. The latter assignments are generally based on relatively small differences between the g values in tetragonal and orthorhombic spectral patterns; the poor resolution of the signals observed here prevents unambiguous assignment.

EXPERIMENTAL

Materials

Solvents and reagents were the highest grade available and were found to be sufficiently pure for use as supplied. Where necessary, solvents were dried by standard procedures.

Physical Techniques

^1H and ^{13}C NMR spectra were recorded with either a QE 300 Plus or a Bruker DRX400 spectrometer. IR spectra were recorded as KBr discs using a Perkin Elmer 1600FTIR spectrometer. Electronic spectra were recorded using a Hewlett Packard 84552 diode array spectrometer with an 89500 UV/vis Hewlett Packard ChemStation. Mass spectra (fast atom bombardment) were obtained using a VG ZAB HS spectrometer equipped with a xenon gun, several matrices were used, including NBA (nitrobenzyl alcohol) and TG/G (thioglycerol/glycerol). ESR spectra were recorded on a Bruker ESP300E spectrometer operating in the X band.

Electrochemical experiments were performed on a Princeton Applied Research Model 175 programmer and Model 173 potentiostat. The output was recorded on paper using a Houston Instruments recorder. A glassy carbon electrode, a silver wire, and a platinum wire were used as working, reference and secondary electrodes, respectively. Under nitrogen, acetonitrile solutions of the complexes (1 mM) with tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte were used in the experiments. The potentials *vs.* SHE were determined using ferrocene as either an internal or external reference.

Magnetic susceptibilities were determined by Evans' method [14] on a QE 300 Plus NMR instrument. Several milligrams of the appropriate complex was dissolved in 0.5 ml of deuterated acetonitrile (containing 1% TMS) in an NMR tube. Then an inner tube with a narrow end containing the blank solvent was inserted into the solution containing the complex. The paramagnetic solute caused the resonance of the TMS peak to shift downfield compared to the sample in the inner tube. Diamagnetic corrections were made using Pascals' constants.

Synthesis of 1,5,9,13-tetraazatetracyclo[11.2.2.2 [5, 9]]heptadecane [4]

1,4,8,12-tetraazacyclopentadecane (prepared by a literature procedure [15]) (8 g, 37.4 mmol) was suspended in acetonitrile (60 mL) and to this was added glyoxal (6 g of a 40% aqueous solution). The reaction mixture was then heated at 65°C for 2 hours. The acetonitrile was removed under reduced pressure and the residue dissolved in water (10 mL). The product was extracted with chloroform (5 x 50 mL), the combined organic extracts dried over anhydrous sodium sulfate and then filtered, followed by removal of the solvent under reduced pressure. The oily residue was distilled under reduced pressure (110°C, 0.01 mmHg), and on standing the product crystallized as white crystals. Yield = 7.6 g (87%). Anal. Calc. for $C_{13}H_{24}N_4$: C, 66.05; H, 10.24; N, 23.71. Found C, 66.20; H, 10.43; N, 24.00. A mass spectrum displayed the expected molecular ion peak [for $C_{13}H_{25}N_4]^+$ at $m/z = 237$. The ^1H NMR (400 MHz, $CDCl_3$) spectrum exhibited peaks at $\delta = 1.29$ (br, 2H), 1.51 (br, 2H), 1.81 (*m*, 1H), 2.06 (*m*, 2H), 2.22 (*m*, 2H), 2.45 (*m*, 6H), 2.74 (*m*, 2H), 2.87 (*m*, 4H), 3.19 (br, 2H), 3.31 (br, 2H). The ^{13}C NMR (100 MHz, $CDCl_3$) spectrum exhibited peaks at $\delta = 20.93$, 23.42, 50.14, 55.08, 56.07.

Synthesis of 5,8-dimethyl-1,5,8,12-tetraazabicyclo[10.3.2]heptadecane(L_1)

1,5,9,13-tetraazatetracyclo[11.2.2.2 [5, 9]]heptadecane (6 g, 25.4 mmol) was dissolved in acetonitrile (200 mL) under a nitrogen atmosphere. To this was added dimethyl sulfate (36 ml, 390 mmol) and the reaction mixture stirred at room temperature for 3 days, yielding a golden brown solution. The acetonitrile was removed under reduced pressure leaving an oily residue. This was stirred with ethyl acetate (3 × 100 mL, 30 minutes), before decanting to remove the excess dimethyl sulfate. This produced a brown solid which was dried under high vacuum for 24 hours. The brown solid was dissolved in ethanol (95%, 300 ml) under nitrogen. Sodium borohydride (14.5 g, 384 mmol) was added slowly to this solution and the reaction mixture stirred at room temperature for 3 days. The remaining sodium borohydride was then cautiously destroyed by the addition of hydrochloric acid (10%) until the pH was between 1 and 2. Ethanol (100%, 100 mL) was added and the organic solvent removed under reduced pressure. The aqueous layer was then made basic (pH = 14), by the addition of potassium hydroxide solution (30%, 250 mL). After extraction with benzene (6 × 100 ml), the combined organic extracts were dried over anhydrous sodium sulfate, before filtration followed by removal of the solvent under reduced pressure. The residue was then distilled over potassium hydroxide pellets under reduced pressure (105°C, 0.01 mmHg) to yield a colorless oil. Yield = 2.08 g (61%). A mass spectrum exhibited the expected molecular ion peak [for $C_{15}H_{33}N_4$]$^+$ at $m/z = 269$. The ^1H NMR (400 MHz, C_6D_6) spectrum exhibited peaks at $\delta = 1.23$ (*m*, 2H), 1.41 (*m*, 2H), 1.79 (*m*, 2H), 1.87 (*s*, 6H), 2.02 (*m*, 2H), 2.17 (*m*, 2H), 2.30 (*m*, 8H), 2.51 (*m*, 4H), 2.72 (*m*, 2H), 2.90 (*m*, 2H). The ^{13}C NMR (100 MHz, C_6D_6) exhibited peaks at $\delta = 26.60$, 30.41, 43.83, 51.81, 53.28, 55.45, 56.33, 56.85.

Complexation Reactions

All metal complex formation reactions were performed under dry nitrogen in a Vacuum Atmospheres Corp. (VAC) glovebox, equipped with a gas circulation and oxygen removal system (VAC M040-1 dry train). Oxygen concentrations were maintained at or below 1 ppm.

Synthesis of MnL_1(SCN)$_2$

Bis(pyridine)manganese(II) chloride was prepared according to a literature procedure [16]. The ligand L_1 (0.42 g, 1.6 mmol) was dissolved in acetonitrile

(6 mL) and to this was added bis(pyridine)manganese(II) chloride (0.455 g, 1.6 mmol), followed by sodium thiocyanate (0.324 g, 4 mmol). The reaction mixture was stirred for 1 hr and then filtered to remove sodium chloride. Ethanol (1 ml) was added to the filtrate and left to evaporate overnight to yield a colorless crystalline solid. Yield = 0.35 g (80%). Anal. Calc. for $Mn_1C_{17}H_{32}N_6S_2$: C, 46.45; H, 7.34; N, 19.13. Found C, 46.70; H, 7.28; N, 19.30. A mass spectrum exhibited the expected molecular ion peak [for $Mn_1C_{16}H_{32}N_5S_1]^+$ at $m/z = 381$. The IR spectrum (KBr disc) showed a strong peak at 2062 and a weaker peak at 773 cm^{-1} (SCN^-). Slow evaporation of an acetonitrile solution of the complex provided crystals suitable for study by X-ray crystallography.

Synthesis of $FeL_1(SCN)_2 \cdot H_2O$

Bis(pyridine)iron(II) chloride was prepared according to a literature procedure [17]. The ligand L_1 (0.42 g, 1.6 mmol) was dissolved in acetonitrile (6 ml) and to this was added bis(pyridine)iron(II) chloride (0.455 g, 1.6 mmol) followed by sodium thiocyanate (0.324 g, 4 mmol). The reaction mixture was stirred for one hour and then filtered to remove sodium chloride. Ethanol (1 ml) and methanol (1 ml) were added to the filtrate and this was then left to evaporate overnight to yield a white crystalline solid. Yield = 0.42 g (60%). Anal. Calc. for $Fe_1C_{17}H_{34}N_6S_2O_1$: C, 44.53; H, 7.48; N, 18.34. Found C, 44.68; H, 7.00; N, 18.68. The mass spectrum displayed the expected molecular ion peak [for $Fe_1C_{16}H_{32}N_5S_1]^+$ at $m/z = 382$. The ^1H NMR (400 MHz, $C_5D_5N_1$) spectrum exhibited peaks at $\delta = 2.55$ (*m*, 2H), 2.74 (*m*, 2H), 3.15 (*m*, 2H), 3.23 (*s*, 6H), 3.35 (*m*, 2H), 3.50 (*m*, 2H), 3.50 (*m*, 2H), 3.60 (*m*, 4H), 3.70 (*m*, 2H), 3.82 (*m*, 2H), 3.92 (*m*, 2H), 4.07 (*m*, 2H) and 4.22 (*m*, *h*). The ^{13}C NMR (100 MHz, $C_5D_5N_1$) spectrum exhibited peaks at $\delta = 27.56$, 31.40, 31.77, 45.07, 52.70, 54.24, 56.53, 57.31 and 57.66. The IR spectrum (KBr disc) showed a strong peak at 2061 cm^{-1} and a weaker peak at 802 cm^{-1} (SCN^-).

CRYSTAL STRUCTURE ANALYSIS

Data Collection and Processing

For crystal data, see Table III. A Siemens SMART [18] three-circle system with CCD area detector, using Mo-Kα radiation (λ 0.71073 Å) was used. Cell parameters were determined by least-squares fitting to numerous

TABLE III Crystal data

Empirical Formula	$C_{17}H_{32}MnN_6S_2$
Formula weight	439.5
Temperature/K	180(2)
Crystal system	Orthorhombic
Space group	Pbca
a/Å	13.791(1)
b/Å	19.088(1)
c/Å	32.657(3)
Volume/Å^3, Z	8597.0(3), 16
Cell determining refls	5604
D(cal)/Mg/m^3	1.357
F(000)	3720
μ(MoK-α)/mm^{-1}	0.822
Crystal dimensions/mm	
θ-max	25
HKL ranges	−15/15, −25/2, −22/36.
Reflections total	12,300
Unique, R(int)	5262, 0.061
With $I > 2\sigma(I)$	3714
Transmission factors	0.80–0.92
Parameters, restraints	473,0
Weighting parameters a, b	0.0350, 27.00
Largest δF peaks/e.Å^{-3}	0.529, −0.268
Goodness-of-fit (F^2)	1.068
$R1$ [$I > 2\sigma(I)$]	0.0558
$wR2$ (all refls)	0.1334

reflection positions. Temperature control was with the Oxford Cryosystem Cryostream Cooler [19]. Absorption correction was done by psi-scan and crystal decay was checked by repeating the initial frames at the end of the collection; the crystals showed no decay.

Structure Analysis and Refinement

The systematic absences indicated the space group uniquely. The structure was solved by direct methods using SHELXS [20] (TREF) with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

Refinement was on F^2 (all reflections) using SHELXL-96 [21]. The weighting scheme was calculated by $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ where $P = (Fo^2 + 2Fc^2)/3$.

Supplementary material available comprises atom coordinates, thermal parameters and full bond lengths and angles.

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