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ELECTROCHEMICAL SYNTHESIS OF MANGANESE(II) COMPLEXES OF PYRIMIDINE-2-THIONES: THE CRYSTAL STRUCTURES OF BIS-4,6-DIMETHYLPYRIMIDYL-2-2′-DISULPHIDE AND 1,10-PHENANTHROLINE-BIS (4,6-DIMETHYLPYRIMIDINE-2-THIOLATO)MANGANESE(II)

JESUS A. CASTRO, JAIME ROMERO, JOSE A. GARCIA-VAZQUEZ, ALFONSO CASTIÑEIRAS and ANTONIO SOUSA*

Departamento de Química Inorgánica, Universidad de Santiago, 15706-Santiago de Compostela, Spain

and

JON ZUBIETA

Department of Chemistry, Syracuse University, Syracuse, NY 13244, U.S.A.

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Abstract—The electrochemical oxidation of anodic manganese in an acetonitrile solution of pyrimidine-2-thione (pymtH) or 4,6-dimethylpyrimidine-2-thione (4,6-Me_2pymtH) and nitrogen donor bidentate ligands such as 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy), yielded mixed complexes [Mn(pymt)$_2$phen], [Mn(4,6-Me_2pymt)$_2$phen] and [Mn(4,6-Me_2pymt)$_2$bipy]. The crystal structures of bis-4,6-dimethylpyrimidyl-2-2′disulphide and 1,10-phenanthroline-bis-(4,6-dimethylpyrimidine-2-thiolato)manganese(II) have been determined by X-ray diffraction. In the manganese complex the metal has a distorted octahedral *trans*-MnS_2N_4 geometry with one nitrogen atom of each pyrimidine ligand uncoordinated.

Metallic complexes of heterocyclic thiones have been thoroughly studied as a consequence of their applications. Recently, the synthesis and structural characterization of *trans*-{dichlorotetraquis-[2(1H)-pyridinethione]}manganese(II) has been described.[1]

However, the chemistry of manganese derivatives of this type of ligand, and in general of thiolates, remains comparatively undeveloped.

For this reason and as a result of our interest in metallic complexes of heterocyclic thiones, we have studied the synthesis of manganese compounds with pyrimidine-2-thione (pymtH) and 4,6-dimethylpyrimidine-2-thione (4,6-Me_2pymtH) using an electrochemical procedure where manganese metal is the anode of a cell containing the ligand in solution. This method has been succesfully used for the synthesis of metallic complexes with heterocyclic thione.[2] However, it has been found that when the thione compound is the only ligand in the solution, the manganese complex is not produced, because oxidation of the ligand to the disulphide occurs. The crystal structure of one such disulphide, (4,6-Me_2pymt)$_2$, has been determined by X-ray diffraction studies. In contrast, when the solution contains additional ligands, such as 1,10 phenanthroline or 2,2′ bipyridine, oxidation of the metal occurs and mixed complexes such as [Mn(pymt)$_2$phen], [Mn(4,6-Me_2pymt)$_2$phen] and [Mn(4,6-Me_2 pymt)$_2$bipy] can been isolated. The crystal structure of [Mn(4,6-Me_2pymt)$_2$phen] has been solved by X-ray diffraction.

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*Author to whom correspondence should be addressed.

EXPERIMENTAL

Acetonitrile, pyrimidine-2-thione (pymtH), 4,6-dimethylpyrimidine-2-thione (4,6-Me_2pymtH), 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) were commercial products and were used without further purification. Manganese (Strem Chemicals) was used as plates.

Preparation of the complexes

The electrochemical procedure employed in the synthesis was similar to that described previously by Tuck.[3] The cell was a tall-form beaker with a rubber bung through which the electrochemical leads entered into the cell. The manganese anode was suspended from a platinum wire in a solution of the corresponding thione in acetonitrile, and in the synthesis of mixed complexes, the appropriate coligand 1,10-phenanthroline or 2,2′-bipyridine was added to the solution. Another platinum wire was the cathode. Direct current was obtained from a purpose built d.c. power supply. The cells can be summarized as:

$$\mathrm{Pt}(-)/\mathrm{CH_3CN}+\mathrm{LH}/\mathrm{Mn}(+)$$

$$\mathrm{Pt}(-)/\mathrm{CH_3CN}+\mathrm{LH}+\mathrm{L'}/\mathrm{Mn}(+)$$

$$\mathrm{LH} = \mathrm{pymtH}, 4,6\text{-}\mathrm{Me_2pymtH}$$

$$\mathrm{L'} = \mathrm{phen\ or\ bipy}.$$

[(4,6-Me_2pymt)$_2$]. An acetonitrile solution (50 cm^3) containing 4,6-dimethylpyrimidine-2-thione (0.75 g) was electrolysed using a 20 mA electric current for 7 h. The colour of the solution was unchanged during the experiment and the amount of the metal passing to the solution was negligible. Concentration of the final solution produced white crystals of [4,6-Me_2pymt]$_2$ suitable for X-ray diffraction studies. Found: C, 51.8; N, 20.8; H, 5.5; S, 24.1. Calc. for (4,6-Me_2pymt)$_2$: C, 51.8; N, 20.1; H, 5.0; S, 23.0%.

[Mn(pymt)$_2$phen]. Electrolysis of an acetonitrile solution (50 cm^3) containing pyrimidine-2-thione (0.28 g) and 1,10-phenanthroline (0.15 g) at 15 V and 20 mA for 2 h dissolved 46 mg of manganese ($E_f = 0.53$). At the end of the experiment, the final solution was left overnight at room temperature under a current of nitrogen. This produced a microcrystalline solid identified as [Mn(pymt)$_2$·phen]·H_2O. Found: C, 49.8; N, 17.6; H, 3.0; S, 13.5. Calc. for [Mn(pymt)$_2$phen·H_2O]: C, 50.5; N, 17.6; H, 3.3; S, 13.5%.

[Mn(4,6-Me_2pymt)$_2$phen]. The electrochemical oxidation of manganese in an acetonitrile solution (50 cm^3) containing 4,6-dimethylpyrimidine-2-thione (0.50 g) and 1,10-phenanthroline (0.25 g) using an 20 mA electric current for 3 h resulted in the dissolution of 64 mg of metal ($E_f = 0.52$). As the reaction proceeds the solution colour changed from colourless to brown–red. From this solution crystals of [Mn(4,6-Me_2pymt)$_2$phen] suitable for X-ray diffraction studies were isolated. Found: C, 56.1; N, 16.3; H, 4.9; S, 13.2. Calc. for [Mn(4,6-Me_2pymt)$_2$phen]: C, 56.1; N, 16.3; H, 4.3; S, 12.7%.

[Mn(4,6-Me_2pymt)$_2$bipy]. Electrolysis of an acetonitrile solution (50 cm^3) containing 4,6-dimethylpyrimidine-2-thione (0.5 g) and bipyridine (0.25 g) using a 20 mA electric current for 3 h caused the dissolution of 62 mg of manganese ($E_f = 0.50$). Crystals of [Mn(4,6-Me_2pymt)$_2$bipy·H_2O] were isolated from the final solution. Found: C, 51.8; N, 17.0; H, 4.4; S, 12.8. Calc. for [Mn(4,6-Me_2pymt)$_2$bipy·H_2O]: C, 52.0; N, 16.7; H, 4.7; S, 12.6%.

Physical measurements

Microanalyses were performed on a Carlo-Erba EA 1108 microanalyser. IR spectra were recorded in KBr mulls using a Perkin–Elmer 180 spectrophotometer.

Crystal structure determination

Crystal data for 4,6-*dimethylpyrimidyldisulphide* (**1**). $C_{12}H_{14}N_4S_2$; $M = 278.40$, colourless prismatic crystal with approximate dimensions $0.10 \times 0.20 \times 0.25$ mm; monoclinic, space group $P2_1/c$, $a = 13.269(7)$, $b = 9.081(1)$, $c = 12.271(6)$ Å, $\beta = 107.58(2)^\circ$, $V = 1409.5(9)$ Å^3, $Z = 4$, $D_c = 1.312$ g cm^{-3}, $F(000) = 584$, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu = 0.358$ mm^{-1}.

Crystal data for [Mn(4,6-Me_2pymt)$_2$phen] (**2**). $C_{24}H_{22}N_6MnS_2$, $M = 513.55$, amber prismatic crystal with approximate dimensions $0.15 \times 0.25 \times 0.30$ mm; monoclinic, space group $P2_1/n$, $a = 13.371(3)$, $b = 11.434(2)$, $c = 16.488(4)$ Å, $\beta = 105.96(1)^\circ$, $V = 2423.6(8)$ Å^3, $Z = 4$, $D_c = 1.407$ g cm^{-3}, $F(000) = 1060$, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu = 0.712$ mm^{-1}.

Data collection and processing

Crystals of both compounds were mounted on glass rods and used for all X-ray experiments, which were carried out on an Enraf–Nonius CAD4 diffractometer at room temperature with Mo-K_α radiation. The lattice parameters were refined using 25 reflections in the range $\theta = 7$–12° for **1** and 8–12° for **2**. Data were collected using the $\omega/2\theta$ technique at $\theta = 3$–29° in **1** and 3–28° in **2**. During the data collection three intensity control reflections have been monitored every 2 h showing no loss of intensity.

Solution and refinement of the structures

Both structures were solved by direct methods.[4] Refinement by the full-matrix least-squares based on F with the weighting scheme[5] of $w = 1/\sigma^2(F)$ of the structural model including all non-H atoms with isotropic displacement parameters, converged at $R = 0.128$ (**1**) and $R = 0.102$ (**2**). An empirical absorption correction with the program DIFABS[6] and merging improved the R values to 0.102 (**1**) and 0.083 (**2**). Upon assignment of anisotropic displacement parameters to all non-H atoms, the residuals were calculated as $R = 0.061$ (**1**) and $R = 0.059$ (**2**). In the disulphide structure the positions of the hydrogen atoms were obtained by difference Fourier synthesis and in the manganese complex were positioned according to idealized geometry (C—H = 0.95 Å). A refinement with anisotropic displacement factors for all non-hydrogen atoms and the position of the H atoms included in structure factor calculations with $B_{iso} = 4.0$ Å^2 (**1**) and $B_{iso} = 5.0$ Å^2 (**2**) fixed but not refined, including a secondary extinction correction[7] in the last cycle of the refinement, converged to the final R values of 0.051 and $Rw = 0.052$ (**1**) and $R = 0.053$ and $Rw = 0.057$ (**2**). All the calculations were carried out on a DECMicrovaxII. The atomic scattering factors were taken from *International Tables*.[8] Molecular graphics from SCHAKAL.[9] Atom positions, bond lengths and bond angles, and other crystallographic data have been deposited as supplementary material.

RESULTS AND DISCUSSION

The electrochemical oxidation of Mn metal anode in an acetonitrile solution of the corresponding pyrimidine-2-thione ligand (HL) and an additional bidentate ligand such as 1,10-phenanthroline or 2,2′-bipyridine (L′) proved to be a convenient one-step route to mixed complexes MnLL′. The average E_f (number of moles of metal dissolved per Faraday of charge) was near to 0.5. This fact and the formation of hydrogen at the cathode are in keeping with the following mechanism.

$$\text{cathode:}\quad 2HL + 2e^- \longrightarrow H_2 + 2L^-$$

$$\text{anode:}\quad 2L^- + Mn + L' \longrightarrow MnL_2L' + 2e^-.$$

When the coligand is not present, oxidation of the metal is not observed, and oxidation of the thione to the disulphide takes place instead.

Molecular structure of [4,6-Me_2pymt]$_2$

Figure 1 shows a perspective view of the molecule with the atomic numbering scheme used. Bond lengths and angles are listed in Table 1. The molecular structure is similar to those of other related organic disulphides, such as bis-pyrimidyl-2-2′-disulphide dihydrate[10] or bis-2-pyridyl disulphide.[11] The molecule shows an equatorial conformation, with an torsion angle C(11)S(1)S(2)C(12) of 94.9°(1), which is within the 90 ± 10° range found in the case of organic disulphides. The torsion angles N—C—S—S are 178.2(2) and −0.7(3)°. This shows that the sulphur atoms and the pyrimidine rings to which they are bound are coplanar. The pyrimidine rings are almost perpendicular, with a dihedral angle of 96.9(1)°.

The S—S bond length, 2.017(1) Å, is almost equal to the distance observed in the above mentioned disulphides, 2.016(2) Å, and close to the average value, 2.03 Å, suggested for organic disulphides. On the other hand, the C—S bond lengths, 1.782(3) and 1.783(3) Å, are close to the values 1.781(2) and 1.785(2) Å found in the above mentioned disulphides, but significatively longer than the bond distance observed in monomer heterocyclic thiones, 1.692(2) Å in the case of pyridine-2-thione.[12] This shows the important contribution of the thione form in the last compound.

Structure of [Mn(4,6-Me_2pymt)$_2$phen]

Figure 2 shows a perspective view of the molecule. Bond distances and angles are listed in Table 2. The manganese atom is bonded to a phenanthroline molecule and two 4,6-dimethylpyridine-2-thionato ligands bonded to the metal through a sulphur and one nitrogen atom of the ring. The environment around the manganese centre is [MnN_4S_2], with the sulphur atoms mutually *trans*.

The geometry of the molecule is a highly distorted octahedron. As a result of the small bite angle of the ligands, the bond angles involving the central atom and mutually *trans* donors differs significantly from the theoretical value of 180°, S(1)MnS(2) is 168.91(9) and N(21)MnN(30) and N(40)MnN(11) are 150.5(3) and 151.1(2)° respectively. As a result, the four equatorial nitrogen atoms are not coplanar. Two of them, N(11) and N(40) respectively, are 0.354(6) and 0.479(6) Å above and the other two, N(21) and N(30) respectively, 0.326(7) and 0.507(6) Å below the best plane determined by

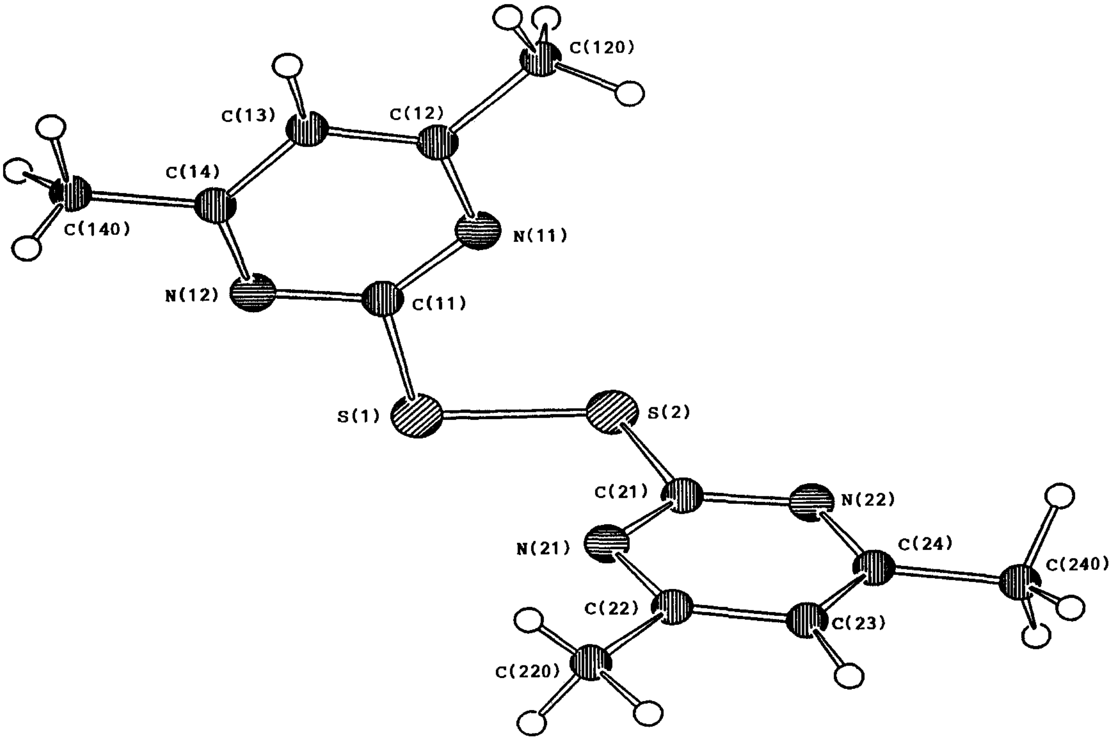

Fig. 1. Molecular structure of $[4,6\text{-}Me_2pymt]_2$.

Table 1. Bond distances (Å) and angles (°) for $(4,6\text{-}Me_2pymt)_2$

Distances			
S(1)—S(2)	2.017(1)	N(22)—C(21)	1.325(4)
S(1)—C(11)	1.782(3)	N(22)—C(24)	1.339(5)
S(2)—C(21)	1.783(3)	C(12)—C(13)	1.372(5)
N(11)—C(11)	1.324(4)	C(12)—C(120)	1.501(5)
N(12)—C(11)	1.327(4)	C(13)—C(14)	1.376(5)
N(12)—C(14)	1.344(4)	C(14)—C(140)	1.491(6)
N(21)—C(21)	1.317(5)	C(22)—C(23)	1.381(5)
N(21)—C(22)	1.349(5)	C(22)—C(220)	1.490(6)
N(11)—C(12)	1.347(5)	C(23)—C(24)	1.373(6)
C(24)—C(240)	1.492(5)		
Angles			
S(2)—S(1)—C(11)	105.3(1)	C(13)—C(14)—C(140)	122.8(3)
S(1)—S(2)—C(21)	105.8(1)	S(2)—C(21)—N(21)	120.4(2)
C(11)—N(11)—C(12)	114.6(3)	S(2)—C(21)—N(22)	110.5(3)
C(11)—N(12)—C(14)	115.2(3)	N(21)—C(21)—N(22)	129.1(3)
C(21)—N(21)—C(22)	114.4(3)	N(21)—C(22)—C(23)	121.7(3)
C(21)—N(22)—C(24)	115.5(3)	N(21)—C(22)—C(220)	116.5(4)
S(1)—C(11)—N(11)	120.8(2)	C(23)—C(22)—C(220)	121.8(3)
S(1)—C(11)—N(12)	110.2(2)	C(22)—C(23)—C(24)	118.2(3)
N(11)—C(11)—N(12)	129.0(3)	N(22)—C(24)—C(23)	121.2(3)
N(11)—C(12)—C(13)	121.5(3)	N(22)—C(24)—C(240)	116.5(4)
C(23)—C(24)—C(240)	122.3(3)	N(11)—C(12)—C(120)	116.3(4)
C(13)—C(12)—C(120)	122.1(4)	C(12)—C(13)—C(14)	118.9(4)
N(12)—C(14)—C(13)	120.8(3)	N(12)—C(14)—C(140)	116.5(3)

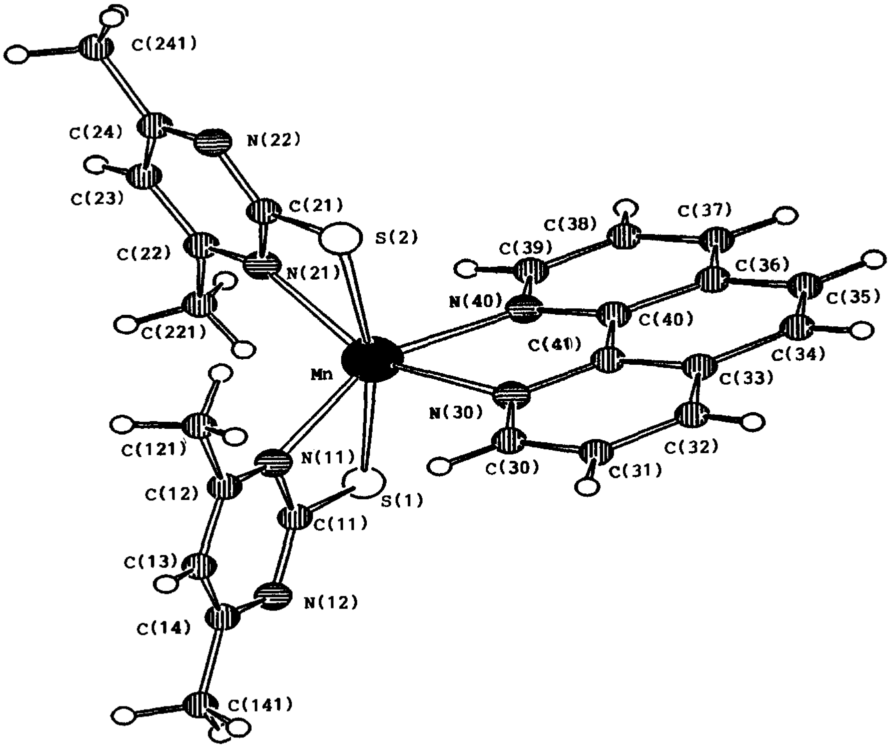

Fig. 2. Molecular structure of [Mn(4,6-Me$_2$pymt)$_2$phen].

these atoms and the metallic atom. The manganese atom is 0.067(1) Å above this plane.

The Mn—S bond distances are essentially identical, 2.594(3) and 2.591(3) Å, but significantly shorter than those found in *trans*-{dichlorotetraquis[2(1H)-pyridinethione]}manganese(II),[1] 2.84(1) and 2.656(1) Å. In this case the ligand is bonded to the manganese centre through the sulphur atom in the thione form. The Mn—S bond distances of the title complex are closer to those found in hexacoordinate manganese complexes with thiolate ligands; for example, in the case of [MnLCl(CH$_3$OH)], ((L = 2-[2-(2pyridil)ethylamino]ethanethiolate),[13] the distance Mn—S is 2.559(3) Å.

The four Mn—N bond distances are similar, falling in the range 2.241(6)–2.277(7) Å. These values are within the range 2.100–2.380 Å found for Mn—N bond distances in octahedral complexes: for example 2.224(8), 2.285(3) and 2.263(12) Å in the octahedral [Mn(phen)$_3$]$^{2+}$ cation,[14] and 2.307(5) Å in the case of [Mn(acac)$_2$phen].[15]

Each 4,6-Me$_2$pymt$^-$ ligand is nearly planar with maximum deviations of the carbon and nitrogen atoms of 0.01 Å. In the case of the sulphur atoms these deviations are 0.067(2) and 0.032(2) Å respectively. The C—S bond distances are 1.719(9) and 1.743(8) Å. These values are similar to those found in other complexes containing pyrimidine-2-thionato as ligand and slightly shorter than the value 1.782(9) Å found in the case of the disulphide precursor. This suggests that the ligand coordinates to the manganese atom with a small contribution of the thione form.

The phenanthroline molecule is almost planar, with deviations from the best least-squares plane smaller than 0.08 Å. The bond angle NMnN of 73.3(2)° falls in the range found for other mixed complexes containing heterocyclic thiones and 1,10-phenanthroline: 75.8(2)° in 1,10-phenanthroline-bis(pyridine-2-thionato)zinc(II)[16] and 69.4(3)° in 1,10-phenanthroline-bis(pyrimidine-2-thionato)cadmium(II).[2]

The IR spectra of the three manganese complexes show bands attributable to the coordination of pyrimidine-2-thiolato, suggesting that the coordination must be similar in all cases. Thus the strong non-aromatic ν(C=C) + ν(C=N) stretching band observed in the free ligands over 1620–1610 cm^{-1} is shifted in the complexes to 1570–1575 cm^{-1}. In addition the strong band over 1435 cm^{-1} in the ligands spectra, which has been attributed to ring vibrations, appears in the spectra of the complexes at lower wave numbers, in the range 1420–1425

Table 2. Bond distances (Å) and angles (°) for [Mn(4,6-Me$_2$pymt)$_2$phen].

Distances			
Mn—S(1)	2.594(3)	Mn—S(2)	2.591(3)
Mn—N(11)	2.252(6)	Mn—N(21)	2.262(7)
Mn—N(40)	2.241(6)	S(1)—C(11)	1.743(8)
S(2)—C(21)	1.719(9)	N(11)—C(11)	1.33(1)
N(11)—C(12)	1.35(2)	N(12)—C(11)	1.35(2)
N(12)—C(14)	1.36(1)	N(21)—C(21)	1.36(2)
N(21)—C(22)	1.35(1)	N(22)—C(21)	1.33(2)
N(22)—C(24)	1.32(1)	N(30)—C(30)	1.32(2)
N(30)—C(41)	1.37(1)	N(40)—C(39)	1.32(1)
N(40)—C(40)	1.34(2)	C(12)—C(13)	1.38(1)
C(12)—C(121)	1.49(1)	C(13)—C(14)	1.34(1)
C(14)—C(141)	1.50(1)	C(22)—C(23)	1.38(1)
C(22)—C(221)	1.50(3)	C(23)—C(24)	1.34(2)
C(24)—C(241)	1.50(1)	C(30)—C(31)	1.39(1)
C(31)—C(32)	1.37(1)	C(32)—C(33)	1.40(1)
C(33)—C(34)	1.44(1)	C(33)—C(41)	1.41(1)
C(34)—C(35)	1.34(1)	C(35)—C(36)	1.43(1)
C(35)—C(36)	1.43(1)	C(36)—C(37)	1.40(1)
C(36)—C(40)	1.40(1)	C(37)—C(38)	1.38(2)
Angles			
S(1)—Mn—S(2)	168.91(9)	S(1)—Mn—N(11)	64.6(2)
S(1)—Mn—N(21)	109.0(3)	S(1)—Mn—N(30)	99.3(2)
S(1)—Mn—N(40)	94.8(2)	S(2)—Mn—N(11)	108.3(2)
S(2)—Mn—N(21)	64.3(2)	S(2)—Mn—N(30)	88.9(2)
S(2)—Mn—N(40)	94.9(2)	N(11)—Mn—N(21)	109.5(3)
N(11)—Mn—N(30)	89.8(2)	N(11)—Mn—N(40)	151.1(2)
N(21)—Mn—N(30)	150.5(3)	N(21)—Mn—N(40)	95.9(2)
N(30)—Mn—N(40)	73.3(2)	Mn—S(1)—C(11)	78.3(3)
Mn—S(2)—C(21)	80.1(3)	C(11)—N(11)—C(12)	118.1(7)
C(11)—N(12)—C(14)	114.2(7)	C(21)—N(21)—C(22)	115.8(8)
C(21)—N(22)—C(24)	117.6(8)	C(30)—N(30)—C(41)	116.6(7)
C(39)—N(40)—C(40)	118.1(7)	S(1)—C(11)—N(11)	115.5(6)
S(1)—C(11)—N(12)	118.7(6)	N(11)—C(11)—N(12)	125.8(7)
N(11)—C(12)—C(13)	119.7(7)	N(11)—C(12)—C(121)	118.6(8)
N(12)—C(14)—C(13)	123.6(8)	S(2)—C(21)—N(21)	114.5(6)
S(2)—C(21)—N(22)	121.1(7)	N(21)—C(21)—N(22)	124.4(8)
N(21)—C(22)—C(23)	121(1)	N(21)—C(22)—C(221)	116(1)
C(23)—C(22)—C(221)	122(1)	C(22)—C(23)—C(24)	118(2)
N(22)—C(24)—C(23)	122.5(9)	N(22)—C(24)—C(241)	115.7(9)
C(23)—C(24)—C(241)	122(2)	N(30)—C(30)—C(31)	124.7(8)

cm^{-1}. Both shifts are in keeping with the thiolate form of the ligand predominating in the complexes. Bands at *ca* 1510, 854 and 727 cm^{-1} in the 1,10-phenanthroline complexes[17] and at *ca* 765 and 735 cm^{-1} in the 2,2′-bipyridine complexes[17] likewise confirm the coordination of these ligands to the manganese atom. Consequently distorted octahedral geometry is proposed for the three manganese complexes.

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