Manganese(II) Complexes Coordinated by a New Derivative of Bipyridine: 9′-[4,5-Bis(methylthio)-1,3-dithiol-2-ylidene]-4′,5′-diazafluorene

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Manganese(II) complexes with the ligand 9′-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-4′,5′-diazafluorene (L) have been synthesized, and the single-crystal structures of complexes $[Mn(L)_2(H_2O)_2](ClO_4)_2{\cdot}(L)_2{\cdot}2C_2H_5OH{\cdot}2CH_3CN$ (**1**), $[Mn(L)_2Cl_2]{\cdot}1.5CH_2Cl_2$ (**2**) and $[Mn(L)_2(NO_3)_2]$ (**3**) have been characterized. Complex **1** is *trans*-coordinated with N···H–O and S···S contacts, while the other two complexes are *cis*-coordinated with short π···π stacking. Solvent-free powder samples were also obtained and these complexes showed catalytic activity in the decomposition of H_2O_2 in the presence of added imidazole; the perchlorate compound was the most effective.

Introduction

Recent decades have seen considerable interest in the design and synthesis of manganese complexes because of their potential use as magnetic materials[1] and catalysts, such as for the disproportionation of hydrogen peroxide.[2] The role of manganese ions in biological systems has been increasingly recognized,[3] e.g. in manganese superoxide dismutase (MnSOD).[4] 1,10-Phenanthroline, bipyridine and their derivatives are well-known excellent N ligands used in manganese model compounds for biological simulations.[5] Consequently, we became interested in ligands of 9′-(4,5-disubstituted-1,3-dithiol-2-ylidene)-4′,5′-diazafluorenes (L),[6] which include a bipyridine moiety and have a similar structure to 1,10-phenanthroline. These ligands also have a conjugated dithiole moiety that influences the relative energy levels of orbitals compared with those of 1,10-phenanthroline and bipyridine. In this paper, we present the synthesis, crystal structures and catalytic properties of a series of Mn^{II} complexes with this type of ligands, $[Mn(L)_2(H_2O)_2](ClO_4)_2$, $[Mn(L)_2Cl_2]$ and $[Mn(L)_2(NO_3)_2]$. Manganese complexes with such ligands are expected to be a new molecular system.

Results and Discussion

Structural Descriptions

$[Mn(L)_2(H_2O)_2](ClO_4)_2{\cdot}2L{\cdot}2C_2H_5OH{\cdot}2CH_3CN$ (1)

In the crystal structure of compound **1** (see a in Figure 1) the manganese atom is symmetrically chelated by four nitrogen atoms from two ligands L, forming a quasi-planar structure that includes the manganese(II) ion with a mean deviation of 0.1119 Å. Perpendicular to the plane are two coordinated water molecules at *trans*-axial positions. Mn(1)−N(1) and Mn(1)−N(2) distances are 2.321 and 2.283 Å, respectively, and in the perpendicular position the Mn(1)−O(1) distance is 2.171 Å, forming an axial-pressed octahedral geometry. Table 1 lists selected bond lengths, angles and interaction distances for **1**−**3** (shorter than the sum of van der Waals radii).

Compound **1** crystallizes in the triclinic space group with co-crystallized free ligand and solvents. Complex molecules form one layer and two free ligands form another layer (see b in Figure 1). These parallel layers are alternately arranged and are linked with N···H−O hydrogen bonds (2.700 Å) and an S···S contact (3.526 Å). These blocks are further linked to a 1D column structure along the *a* axis by hydrogen bonds between coordinated water molecules and the solvent molecules. There are also short S···S interactions (3.311 Å) between the columns.

$[Mn(L^1)_2Cl_2]{\cdot}1.5CH_2Cl_2$ (2)

Figure 2 (a) shows the X-ray crystal structure of the compound **2**. The complex crystallizes in a monoclinic system with eight complex molecules and 12 dichloromethane molecules in a unit cell. In the crystal structure of **2**, the Mn

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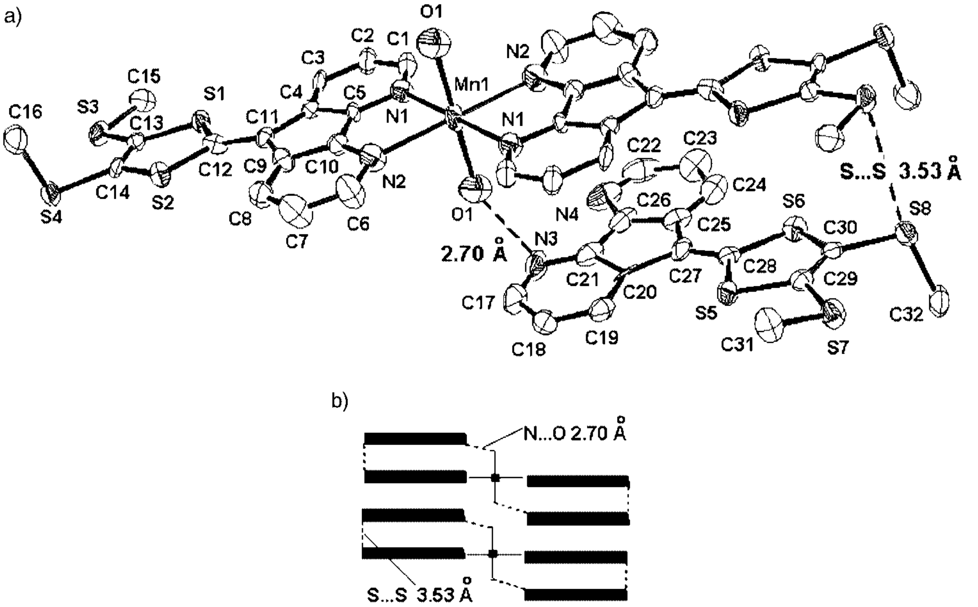

Figure 1. (a) ORTEP view of **1** showing the atom labels; solvents omitted for clarity; (b) schematic view of the layered arrangement of the complex and the co-crystallized free ligand; broken lines show intermolecular interactions

Table 1. Selected bond lengths [Å], angles [°] and interaction distances for **1** − **3**; i: 1 − *x*, −*y*, 1 − *z*; ii: 1 − *x*, −*y*, −*z*; iii: 1/2 − *x*, 1/2 + *y*, 1/2 − *z*; iv: 1/2 + *x*, −*y*, *z*; v: −*x*, 1 − *y*, *z*

1		**2**		**3**	
Mn(1)−O(1)	2.171(9)	Mn(1)−Cl(1)	2.458(2)	Mn(1)−O(1)	2.113(5)
Mn(1)−N(1)	2.32(1)	Mn(1)−Cl(2)	2.425(2)	Mn(1)−O(4)	2.118(3)
Mn(1)−N(2)	2.282(9)	Mn(1)−N(1)	2.304(5)	Mn(1)−N(1)	2.333(3)
O(1)−Mn(1)−N(1)	93.23	Mn(1)−N(2)	2.422(6)	Mn(1)−N(2)	2.322(3)
O(1)−Mn(1)−N(1′)	86.77	Mn(1)−N(3)	2.431(6)	Mn(1)−N(3)	2.310(4)
O(1)−Mn(1)−N(2)	90.36	Mn(1)−N(4)	2.299(6)	Mn(1)−N(4)	2.340(3)
O(1)−Mn(1)−N(2′)	89.64	Cl(1)−Mn(1)−Cl(2)	99.34(8)	O(1)−Mn(1)−O(4)	84.2(2)
N(1)−Mn(1)−N(2)	78.93	N(1)−Mn(1)−N(2)	75.98	N(1)−Mn(1)−N(2)	78.01
		N(3)−Mn(1)−N(4)	76.50	N(3)−Mn(1)−N(4)	77.69
S(3)···S(8)^{i}	3.526(5)	C(17)···C(7)^{iii}	3.37(1)	C(27)···C(23)^{iv}	3.390(5)
S(7)···S(7)^{ii}	3.311(5)	C(18)···C(6)^{iii}	3.28(1)	C(2)···C(11)^{v}	3.371(7)
O(1)···N(3)	2.70(1)	C(20)···C(8)^{iii}	3.38(1)		
		C(21)···C(8)^{iii}	3.354(9)		

atom also exhibits a six-coordinate environment that consists of the four nitrogen atoms from the two ligands and two *cis* chloride ions, but the geometry is distorted far from formal octahedral. The mean deviation from the plane of the two ligands is 0.0720 and 0.1478 Å, respectively. The dihedral angle between the least-squares planes of the two ligands is 92.671°.

Mn(1)−Cl(1), 2.458 Å, and Mn(1)−Cl(2), 2.425 Å, bond lengths are similar to those of [Mn(phen)$_2$Cl$_2$],[5c] a (dichloro)Mn^{II} complex showing a coordination environment resembling that of **2**. The bonds of Mn(1)−N(3) (2.431 Å) and Mn(1)−N(2) (2.420 Å) *trans* to Cl(1) and Cl(2), are longer than those of Mn(1)−N(1) (2.304 Å) and Mn(1)−N(4) (2.298 Å). This suggests that the axes Cl(1)−Mn(1)−N(3) and Cl(2)−Mn(1)−N(2) are elongated and the octahedral geometry is distorted. There is short π···π stacking between the conjugated ligands (in the range of about 3.3−3.5 Å, Table 1). These interactions and the coordination bonds result in 1D zigzag chains along the *b* axis (Figure 2, b).

[Mn(L^1)$_2$(NO$_3$)$_2$] (3)

Figure 3 (a) shows the X-ray crystal structure of **3**. The complex crystallizes as a monoclinic system with two complex molecules in a unit cell. In the crystal structure of **3**, the coordination environment around the manganese(II) center is a distorted octahedral coordination geometry, like that of **2**. The Mn^{II} ion is coordinated by four nitrogen atoms from two chelating ligands and the two *cis*-oxygen atoms from two nitrate anions. The mean deviation from the plane of the two ligands is 0.0563 and 0.0590 Å, respec-

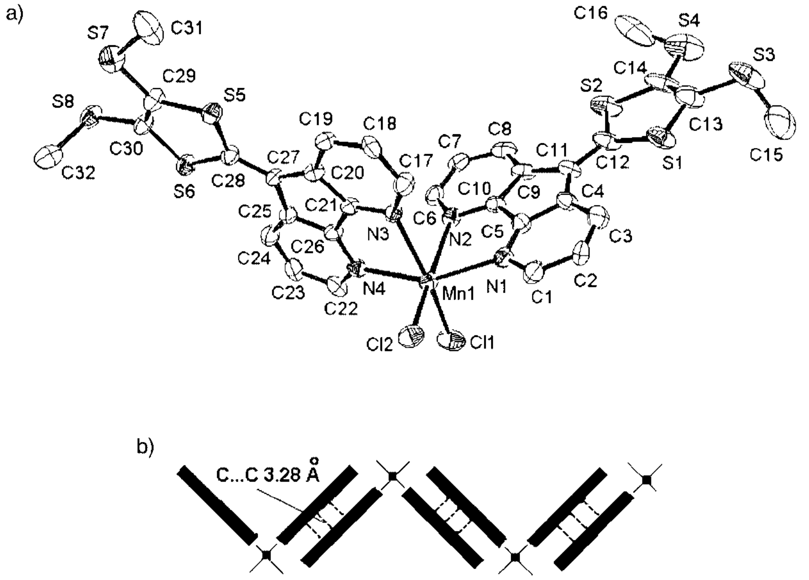

Figure 2. (a) ORTEP view of **2** showing the atom labels; solvents omitted for clarity; (b) schematic view of the 1D arrangement and intermolecular π···π stacking

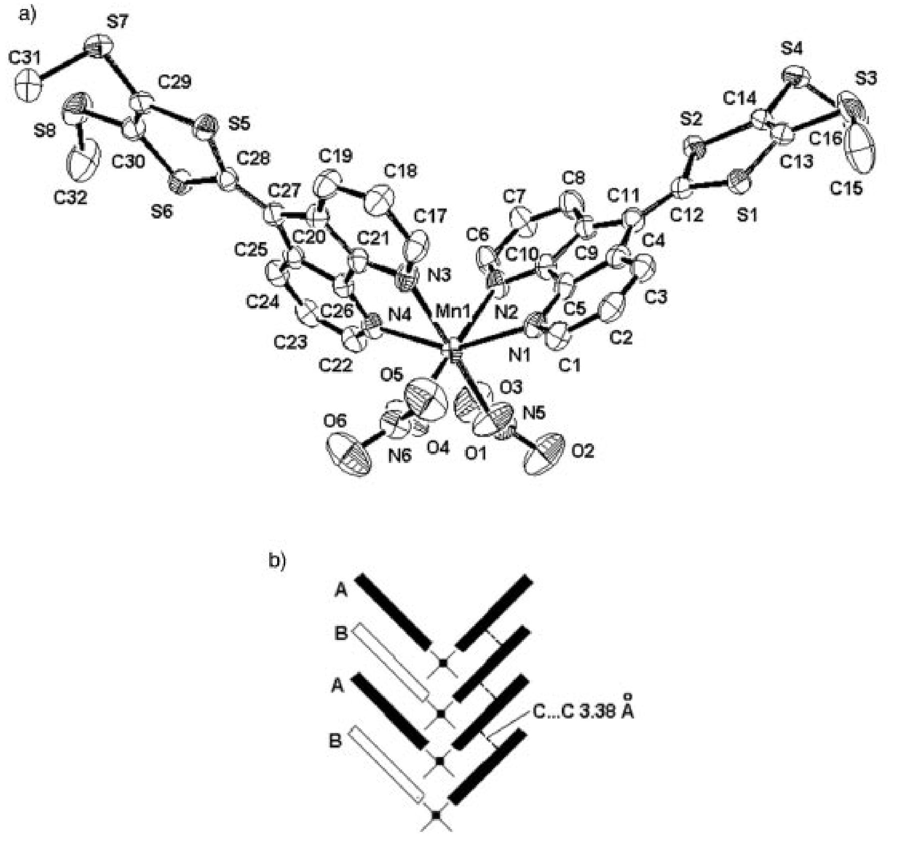

Figure 3. (a) ORTEP view of **3** showing the atom labels; (b) schematic view of molecular packing and π···π stacking; A and B represent ligands orientated in different directions

tively, which are better than those of **2**. The dihedral angle between least-squares planes of the two ligands is 95.09°. The crystal is also stabilized by interligand π···π stacking, but the crystal packing is quite different from that of **2**. Ligand planes from two different symmetrical molecules are arranged alternately with C···C distances of 3.37 or 3.38 Å, forming 1D ligand columns along the *a* axis (Figure 3, b). In Figure 3 (b), A and B represent ligands orientated in different directions and those molecules interact further with others in the same manner as described above (1D ligand columns). By the metal coordination linkage these $\pi\cdots\pi$-assembled ligand columns form a 2D structure parallel with the (001) plane.

Synthesis and Properties

Table 2 gives selected IR vibration bands of the powder samples and their assignments. The shift of the $\nu(C=N)$ band is not very notable for the coordination of Mn^{II}, whereas the $\nu(C=C)$ band at 1488 cm^{-1} for the free ligand L is clearly shifted to lower energy for complexes, due to the metal coordination. In contrast to the C=C bands, the S−C−S vibrations at about 857 cm^{-1} are enhanced. The ClO_4^- and NO_3^- vibrations of the complexes **1′** and **3** at around 1130 and 1442 cm^{-1} confirm the presence of these counterions.

Table 2. Characteristic IR bands of the ligand and its complexes [cm^{-1}]; **1′** and **2′** are solvent-free compounds corresponding to **1** and **2**

Compound	$\nu(C=N)$	$\nu(C=C)$	$\nu(S-C-S)$	Anion
L	1540 vs	1488 vs	857 m	
1′	1538 vs	1478 vs	868 m	1130 vs
2′	1536 vs	1473 vs	867 m	
3	1539 vs	1479 s	868 m	1442 s

Although single crystals suitable for X-ray diffraction were obtained and the structures of **1**−**3** have been successfully determined, the composition of the powder samples of **1′** and **2′** differ from those of the crystals. Crystals of **1** and **2** contain solvent molecules that are easily lost from the powder samples in vacuo. Interestingly, free ligand is not contained in **1′**, unlike crystals of **1**. Both the results of elemental analysis and IR measurement suggest this conclusion. IR spectra of the three powder complexes are essentially the same, except for the band of the anions and no peak splits (for free L) were found for **1′**. Unlike the synthesis of powder **1′**, **1** was obtained by adding some ethanol solvent to the reaction filtrate, which decreased the solubility of the ligand and therefore free L co-crystallized with the molecules of complex and solvents. Owing to the space filling of those free L molecules, **1** has a different structure (C_i) to those of **2** and **3** (C_2) (see Figure 1−3).

To further understand the structure of **1′**, ESR spectra of **1′** and **3** were recorded (Figure 4). A *trans* structure would show an axial field character in the ESR spectra with g values of 2 and 6 for monomeric Mn^{II} complexes,[7] but the ESR patterns of **1′** and **3** do not satisfy an axially symmetric electron environment. A higher rhombic distortion from octahedral geometry can be deduced for the complexes owing to the *cis* instead of *trans* structure. Examples of Mn^{II} complexes have been discussed in detail.[8] The results are in accord with the structure determination of **3**. Since the signal characters of **1′** and **3** are similar, the most promising structure of **1′** is a *cis*-coordination geometry, as in the crystal structures of **2** and **3**.

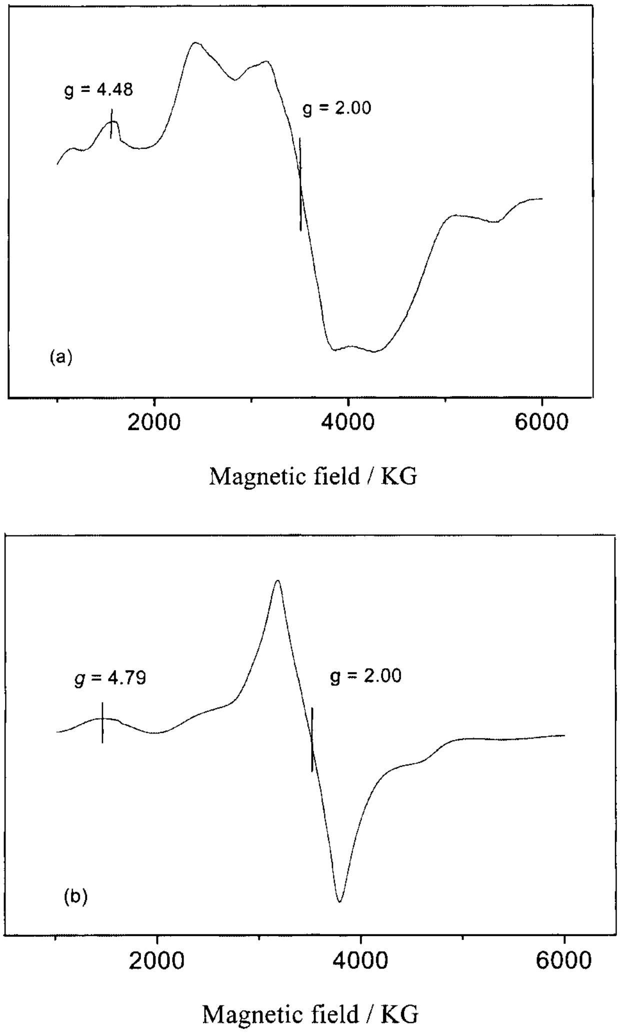

Figure 4. ESR spectra of **1′** (a) and **3** (b) powder samples measured at room temperature

Several manganese(II) complexes have been studied for catalytic activity in decomposing H_2O_2. Since our new ligands are derivatives of bipy and phen (ligands that are widely used in such catalytic systems), it seemed worthwhile to study the catalytic activity of the new Mn^{II} compounds. Unfortunately, unlike Mn^{II} complexes of bipy and phen, compounds **1**−**3** are all insoluble in water; therefore, it is impossible to discuss the influences of the conjugated electron-donor moiety of dithiole on activity by direct comparison with those of bipy or phen complexes. However, catalytic activities of **1**−**3** were determined in a heterogeneous reaction system (Figure 5). All the complexes showed activity for the catalytic decomposition of H_2O_2 in the presence of added imidazole. Among them $[Mn(L)_2(H_2O)_2](ClO_4)_2$ (**1′**) is the most effective. Experiments were repeated several times to ensure consistency of the results. The higher activity of **1′** is attributed to the coordinated water molecules, which are exchangeable in the catalytic system.

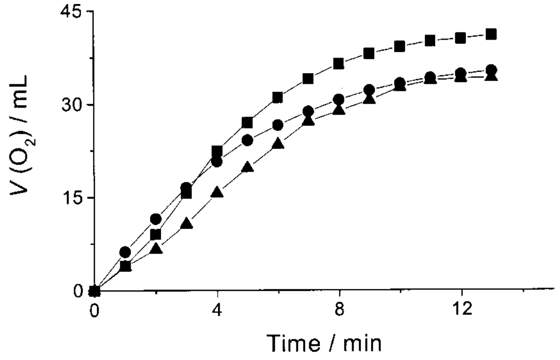

Figure 5. Activity in the catalytic decomposition of H_2O_2 in the presence of imidazole: **1′** (squares), **2′** (triangles) and **3** (circles)

Experimental Section

General Remarks: The ligand L, 9′-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-4′,5′-diazafluorene, was prepared according to ref.[9] Acetonitrile was dried and distilled by a standard method before use. Elemental analyses of C, H and N were performed using an EA1110 elemental analyzer. IR spectra were recorded as KBr discs with a Nicolet Magma 550 FT-IR spectrometer. ESR spectra were recorded with a Jeol-FE1XG spectrometer at room temperature.

Synthesis of Complexes

[Mn(L)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ (1′): A dichloromethane solution (20 mL) of the ligand L (0.1 mmol, 36 mg) was slowly added dropwise to an acetonitrile solution (4 mL) of $Mn(ClO_4)_2\cdot6H_2O$ (0.05 mmol, 18.1 mg). The resultant orange precipitate, formed after the mixture was stirred at room temperature for 30 min, filtered off, washed with acetonitrile and dichloromethane and, finally, dried in vacuo over silica gel (yield: 48 mg, 65%). $C_{32}H_{28}Cl_2MnN_4O_{10}S_8$ (1010.9): calcd. C 38.02, H 2.79, N 5.54; found C 37.96, H 2.87 N 5.69.

[Mn(L)$_2$Cl$_2$] (2′): To an ethanol solution (10 mL) of $MnCl_2\cdot4H_2O$ (0.05 mmol, 10.0 mg) was slowly added dropwise a dichloromethane solution (20 mL) of the ligand L (0.1 mmol, 36 mg). Then, all the procedures were similar to that of **1** (yield: 49 mg, 67%). $C_{32}H_{24}Cl_2MnN_4S_8$ (846.9): calcd. C 45.39, H 2.84, N 6.62; found C 45.27, H 2.78, N 6.56.

[Mn(L)$_2$(NO$_3$)$_2$] (3): A dichloromethane solution (20 mL) of the ligand L (0.1 mmol, 36 mg) was slowly added dropwise to an ethanol solution (5 mL) of $Mn(NO_3)_2$ ca. 0.1 mmol, 20 μL, 50% w/w aqueous solution). Subsequent procedures were similar to that of **1** (yield: 45 mg, 65%). $C_{32}H_{24}MnN_6O_6S_8$ (900.0): calcd. C 42.71, H 2.67, N 9.34; found C 37.12, H 2.38, N 5.49.

[Mn(L)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$·(L)$_2$·2C$_2$H$_5$OH·2CH$_3$CN (1): Crystals of complex **1** was prepared by slowly adding dropwise a dichloromethane solution (10 mL) of the ligand L (0.02 mmol, 7.2 mg) to an acetonitrile solution (3 mL) of $Mn(ClO_4)_2\cdot6H_2O$ (0.01 mmol, 3.62 mg). The resultant mixture was stirred at room temperature for 30 min and then filtered. Ethanol was then gently layered on the filtrate, which was sealed in bottles and left undisturbed at room temperature for several days. The so-obtained orange, single crystals were suitable for X-ray diffraction.

[Mn(L)$_2$Cl$_2$]·1.5CH$_2$Cl$_2$ (2) or Mn(L)$_2$(NO$_3$)$_2$] (3): Crystals of **2** or **3** were prepared in dilute solutions by similar procedures to that above. Filtrates were sealed in bottles and left undisturbed at room temperature for several days to afford orange single crystals suitable for X-ray diffraction.

Hydrogen Peroxide Disproportionation Studies: Aqueous H_2O_2 (2 wt.%, 5 mL) was added to a solid mixture consisting of the complex (2.3×10^{-3} mmol) and imidazole (5 mg). This combination was

Table 3. Crystallographic data for complexes **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{72}H_{68}Cl_2MnN_{10}O_{12}S_{16}$	$C_{33.50}H_{27}Cl_5MnN_4S_8$	$C_{32}H_{24}MnN_6O_6S_8$
Formula mass	1904.19	974.29	900.00
Crystal size [mm]	0.22 × 0.42 × 0.05	0.10 × 0.40 × 0.20	0.70 × 0.15 × 0.30
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	Pa (no. 7)
a [Å]	7.564(2)	25.044(3)	9.113(1)
b [Å]	11.980(4)	16.0260(13)	14.019(2)
c [Å]	24.331(7)	22.654(3)	14.955(2)
α [°]	102.461(13)	90	90
β [°]	92.462(9)	115.720(4)	107.621(7)
γ [°]	100.986(13)	90	90
V [Å^3]	2105.4(11)	8191.8(15)	1820.8(4)
Z	1	8	2
$D_{calcd.}$ [mg·m^{-3}]	1.502	1.580	1.641
F(000)	981.00	3952.00	918.00
$2\theta_{max.}$ [°]	55.0	55.0	55.0
No. of reflections measured	14203	83234	24388
No. of unique reflections	8877	9650	7747
No. of reflections [$I > 3.0\sigma(I)$]	3654	4630	6456
Goodness-of-fit (S)	1.014	1.001	1.011
R_1	0.090	0.063	0.037
wR_2	0.179	0.178	0.104

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$

then stirred and thermostatted at 25 °C. Evolved O_2 was measured volumetrically.

X-ray Crystallographic Study: X-ray crystallographic data for complexes **1**−**3** were obtained using a Rigaku Mercury CCD area detector with graphite-monochromated Mo-K_α ($\lambda = 0.71070$ Å) radiation, at 193 K. Table 3 lists selected crystallographic data for three complexes and details of data collection. An empirical absorption correction was applied and data were corrected for Lorentz and polarization effects. All structures were solved by direct methods[10] and expanded using Fourier techniques.[11] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on observed reflections and variable parameters and converged to unweighted and weighted agreement factors. Calculations were performed using the CrystalStructure software package. CCDC-236214 to -236216 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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