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Synthesis and fungitoxic activity of manganese(II) complexes of fumaric acid: X-ray crystal structures of [Mn(fum)(bipy)(H_2O)] and [Mn(Phen)$_2$(H_2O)$_2$](fum)$\cdot$4H_2O (fumH_2 = fumaric acid; bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline)

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Abstract

The reaction of fumaric acid with Mn(CH_3COO)$_2\cdot$4H_2O gives the polymeric complex $\{$Mn(fum)$\}_n$ (**1**). Complex **1** reacts with 2,2′-bipyridine in ethanol to yield [Mn(fum)(bipy)(H_2O)]$_n$ (**2**). Reaction of **1** with 2 equiv. of 1,10-phenanthroline produces [Mn_2(fum)$_2$(phen)$_{2.5}$]$\cdot$3H_2O (**3**) and [Mn(phen)$_2$(H_2O)$_2$](fum)$\cdot$4H_2O (**4**). The molecular structures of **2** and **4** were determined by X-ray crystallography. In **2** the fumarate anions link the manganese ions so that each is seven coordinate, being bonded to a bidentate bipyridine, two bidentate carboxylates and one H_2O molecule. In **4** the asymmetric unit contains a [Mn(phen)$_2$(H_2O)$_2$]$^{2+}$ cation, half of each of two independent fumarate anions and four lattice H_2O molecules. The cations and anions are interconnected by water molecules hydrogen bonded to both coordinated water molecules and fumarate oxygens. The fumarate complexes, the metal free ligands and a number of simple manganese salts were each tested for their ability to inhibit the growth of *Candida albicans*. Only the 'metal free' 1,10-phenanthroline and its fumarate complexes exhibit fungitoxic activity

Keywords: Manganese(II) complexes; Fumaric acid; Crystal structures; Fungitoxic activity

1. Introduction

The yeast *Candida albicans* is a commensal of the human body and is considered to be an important fungal pathogen. Opportunistic infection can lead to the development of vaginal candidosis (thrush), a condition from which over 75% of women suffer at some stage in their lifetime. Systemic candidosis is often fatal in immunocompromised patients [1–4]. The state-of-the-art drugs currently used to treat *Candida* infections are often ineffective because of problems with resistance or toxicity and subsequently the search for novel anti-fungal agents has gathered momentum [5]. A number of publications has appeared in the literature highlighting the fungicidal activity of novel transition metal complexes, see for example Ref. [6]. Recently, we have shown that a range of cobalt carboxylate complexes inhibit the growth of *Candida albicans* [7]. Whereas metal complexes of aliphatic monocarboxylic acids have been extensively studied, relatively few papers describing the structures of their diacid equivalents have been published [8]. Rarer still are reports documenting the structures of complexes of unsaturated aliphatic diacids. We have previously described the synthesis, X-ray crystal structures and catalytic activity of a number of manganese(II) complexes containing saturated aliphatic α,ω-dicarboxylic acid ligands [9–13]. Herein we report the synthesis and structural characterisation of two new manganese(II) complexes of fumaric acid. In addition the in vitro anti-*Candida* activities of the compounds are discussed.

2. Results and discussion

Synthetic routes to complexes **1–4** are shown in Scheme 1. $\{$Mn(fum)$\}_n$ (**1**) was prepared in high yield by reacting

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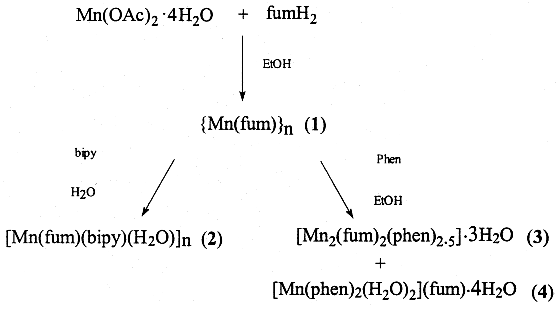

Scheme 1.

manganese(II) acetate tetrahydrate with fumaric acid. Reaction of **1** with excess 2,2′-bipyridine gave $[Mn(fum)(bipy)(H_2O)]_n$ (**2**). When an ethanolic suspension of complex **1** was reacted with 1,10-phenanthroline in a 1:2 molar ratio $[Mn_2(fum)_2(phen)_{2.5}] \cdot 3H_2O$ (**3**) was obtained in high yield. The filtrate from this reaction, when left standing, produced yellow crystals of $[Mn(phen)_2(H_2O)_2](fum) \cdot 4H_2O$ (**4**).

The X-ray structure of **2** is shown in Fig. 1 and selected bond lengths and angles for the complex are given in Tables 1 and 2, respectively. The structure consists of zig-zag polymeric chains running approximately parallel to the *b* axis and in which the monomer is the asymmetric unit $[Mn(fum)(bipy)(H_2O)]$. The *trans*-fumarate anions link the manganese ions so that each is seven coordinate, being bonded to a bidentate bipyridine, two bidentate carboxylates and one H_2O molecule (Fig. 1). The geometry at the manganese ions is quite irregular, the four Mn–O(carboxylate) distances are quite different from each other (Table 1), with that to O(21) being particularly long (2.388(1) Å); unexpectedly, the shortest bond is to the coordinated water molecule (Mn–O1w 2.174(1) Å).

The polymeric chains themselves are linked into sheets in the *ab* plane by hydrogen bonding (Fig. 2) involving coordinated H_2O on one chain and two of the fumarate oxygen atoms on a neighbouring chain (Table 2).

Finally, the two-dimensional sheets are linked by weak π–π stacking of bipyridine groups in adjacent sheets (Fig. 2) (interplanar stacking distance, ∼3.8 Å). This long π–π distance may be enforced by the steric constraints of the relatively rigid fumarate dianion.

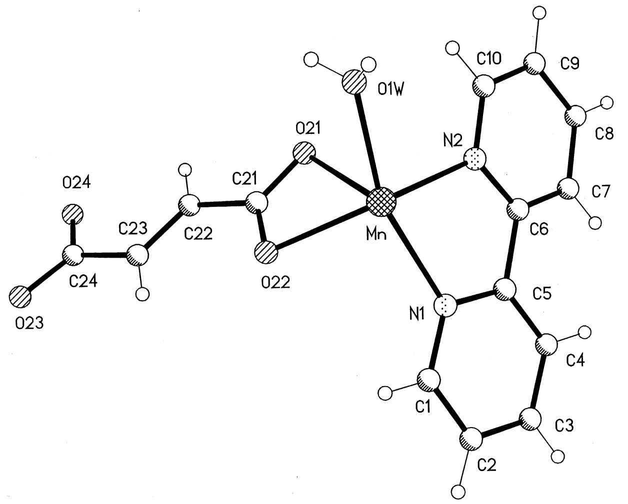

Fig. 1. The asymmetric unit of $[Mn(fum)(bipy)(H_2O)]_n$ (**2**).

Table 1
Selected bond lengths (Å) and angles (°) for complex **2**

Mn–O(1W)	2.1737(14)
Mn–O(22)	2.2473(12)
Mn–N(2)	2.2720(15)
Mn–N(1)	2.2923(15)
Mn–O(24)	2.3036(11)
Mn–O(23)	2.3297(12)
Mn–O(21)	2.3877(13)
O(1W)–Mn–O(22)	105.25(5)
O(1W)–Mn–N(2)	94.16(5)
O(22)–Mn–N(2)	128.96(5)
O(1W)–Mn–N(1)	162.40(5)
O(22)–Mn–N(1)	92.07(5)
N(2)–Mn–N(1)	71.98(5)
O(1W)–Mn–O(24)	96.78(5)
O(22)–Mn–O(24)	83.04(4)
N(2)–Mn–O(24)	141.55(4)
N(1)–Mn–O(24)	88.25(5)
O(1W)–Mn–O(23)	81.90(5)
O(22)–Mn–O(23)	139.94(4)
N(2)–Mn–O(23)	88.61(4)
N(1)–Mn–O(23)	86.86(5)
O(24)–Mn–O(23)	56.90(4)
O(1W)–Mn–O(21)	79.67(5)
N(2)–Mn–O(21)	82.47(4)
N(1)–Mn–O(21)	108.30(5)
O(24)–Mn–O(21)	135.75(4)
O(23)–Mn–O(21)	158.84(5)
O(22)–Mn–O(21)	56.41(4)

The X-ray structure of **4** is shown in Fig. 3 and selected bond lengths and angles are listed in Tables 3 and 4, respectively. The asymmetric unit contains a $[Mn(phen)_2(H_2O)_2]^{2+}$ cation, half of each of two independent fumarate anions and four lattice H_2O molecules. The manganese is six coordinate in a *cis*-conformation. One of the fumarate anions (containing O21 and O22) is hydrogen bonded in a 'bidentate' way to both the coordinated water molecules (O1w and O2w). Since this fumarate lies on a centre of symmetry, it acts as a hydrogen-bonded bridge between two neighbouring cations. The second fumarate anion is linked to the cation via a single hydrogen bond (to O2w); this anion also lies on a centre of symmetry, bridging two cations. The lattice therefore contains polymeric, hydrogen-bonded chains of alternating cations and anions.

The four uncoordinated lattice water molecules show extensive hydrogen bonding, to the anion oxygen atoms, the coordinated water and other lattice water molecules (Fig. 4). This results in a complicated hydrogen-bonded network that extends throughout the lattice. The cations and anions are

Table 2
Hydrogen bond lengths (Å) and angles (°) for complex **2** [a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1W)–H(1WA)···O(22)#1	0.81(2)	1.97(2)	2.7241(17)	155(2)
O(1W)–H(1WB)···O(24)#2	0.83(2)	1.94(2)	2.7057(17)	153(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x+1/2, y, -z+1/2$, #2 $-x+1/2, y+1/2, z$.

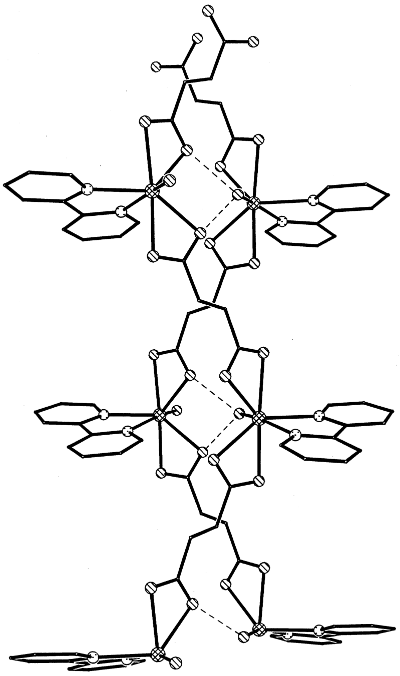

Fig. 2. The polymeric chains in $[\mathrm{Mn(fum)(bipy)(H_2O)}]_n$ (**2**).

interconnected by water molecules hydrogen bonded to both coordinated water molecules and fumarate oxygens.

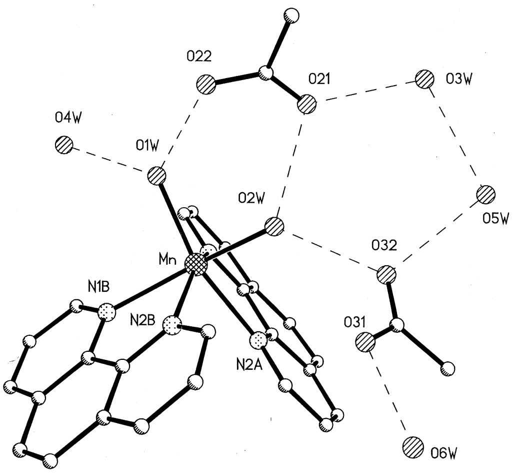

Fig. 3. The asymmetric unit of $[\mathrm{Mn(Phen)_2(H_2O)_2}](\mathrm{fum})\cdot 4\mathrm{H_2O}$ (**4**).

Table 3
Selected bond lengths (Å) and angles (°) for complex **4**

Mn–O(2W)	2.1297(10)
Mn–O(1W)	2.1433(10)
Mn–N(2B)	2.2690(12)
Mn–N(1A)	2.2728(11)
Mn–N(1B)	2.2965(11)
Mn–N(2A)	2.3157(12)
O(2W)–Mn–O(1W)	84.77(4)
O(2W)–Mn–N(2B)	89.32(4)
O(1W)–Mn–N(2B)	108.83(4)
O(2W)–Mn–N(1A)	109.66(4)
O(1W)–Mn–N(1A)	92.98(4)
N(2B)–Mn–N(1A)	152.52(4)
O(2W)–Mn–N(1B)	161.69(4)
O(1W)–Mn–N(1B)	95.47(4)
N(2B)–Mn–N(1B)	73.22(4)
N(1A)–Mn–N(1B)	88.63(4)
O(2W)–Mn–N(2A)	87.96(4)
O(1W)–Mn–N(2A)	161.05(4)
N(2B)–Mn–N(2A)	88.51(4)
N(1A)–Mn–N(2A)	73.04(4)
N(1B)–Mn–N(2A)	96.89(4)

The IR spectrum of **1** contains prominent ν_{OCOasym} and ν_{OCOsym} stretching bands around 1575 and 1387 cm^{-1}, respectively. The relatively large value of Δ_{OCO} ($\nu_{\mathrm{OCOasym}}-\nu_{\mathrm{OCOsym}}$) calculated for the complex (188 cm^{-1}) is close to the value expected for a unidentate coordination mode of the carboxylate moiety [14]. Its relative insolubility in most common solvents suggests that it may have a polymeric structure. Indeed, we have found in previous studies that the saturated aliphatic dicarboxylic acids usually give polymeric complexes when reacted with manganese(II) acetate [9–13]. Complex **1** is sparingly soluble in ethanol and its molar conductivity ($\Lambda_{\mathrm{M}}=0.43$ S cm^2 mol^{-1}) suggests that it is a non-electrolyte in this solvent. The Δ_{OCO} value for complex **2** (114 cm^{-1}) is as expected for a chelating coordination mode of the carboxylate moieties [14]. The molar conductivity value for an aqueous solution of complex **2** ($\Lambda_{\mathrm{M}}=163$ S cm^2 mol^{-1}) suggests that it forms a 1:1 electrolyte in water and dissociates to give the cationic $[\mathrm{Mn(bipy)}]^{2+}$ and the anionic fum^{2-} species, respectively. Complex **3** was isolated as a powder which was only sparingly soluble in methanol and chloroform. The value of Δ_{OCO} ($\nu_{\mathrm{OCOasym}}-\nu_{\mathrm{OCOsym}}$) calculated for the complex (182 cm^{-1}) is similar to that for complex **1**, suggesting that the carboxylate functions may be coordinated to the manganese centres in a similar mode. The molar conductivity value of **3** ($\Lambda_{\mathrm{M}}=1.52$ S cm^2 mol^{-1}) suggests that it does not dissociate in methanol. Although the fumarate ligand is uncoordinated in complex **4** the relatively high Δ_{OCO} value (215 cm^{-1})

Table 4
Hydrogen bond lengths (Å) and angles (°) for complex **4** [a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1W)–H(1WA)···O(22)	0.88	1.87	2.7372(14)	169.9
O(1W)–H(1WB)···O(4W)	0.85	1.87	2.6980(14)	164.4
O(2W)–H(2WA)···O(21)	0.91	1.79	2.6987(14)	175.7
O(2W)–H(2WB)···O(32)	0.88	1.73	2.6184(13)	177.2
O(3W)–H(3WA)···O(21)	0.86	1.96	2.8072(14)	167.5
O(3W)–H(3WB)···O(5W)	0.91	1.92	2.8295(17)	172.8
O(4W)–H(4WA)···O(6W)#1	0.84	1.91	2.7393(16)	170.3
O(4W)–H(4WB)···O(22)#2	0.88	1.86	2.7433(15)	174.0
O(5W)–H(5WA)···O(32)	0.85	1.99	2.8248(15)	167.7
O(5W)–H(5WB)···O(3W)#3	0.77	2.15	2.9089(17)	167.9
O(6W)–H(6WA)···O(3W)#4	0.91	1.93	2.8339(17)	172.2
O(6W)–H(6WB)···O(31)	0.91	1.87	2.7758(16)	177.3

[a] Symmetry transformations used to generate equivalent atoms: #1 $x-1$, $y-1$, z, #2 $-x+1$, $-y$, $-z+1$, #3 $-x+1$, $-y+1$, $-z$, #4 $x+1$, y, z.

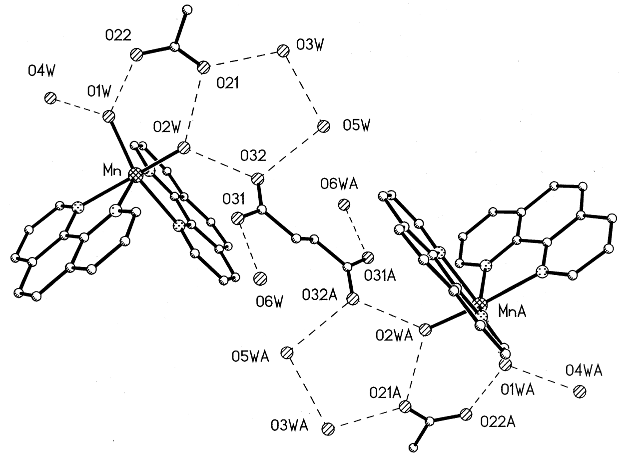

Fig. 4. The structure of $[Mn(Phen)_2(H_2O)_2](fum)\cdot 4H_2O$ (**4**) with hydrogen-bonding interactions.

Table 5
Anti-*Candida* activity [a]

Test compound	% Cell growth Isolate
Control	100
Fumaric acid	106 ± 8
1,10–phenanthroline	23 ± 2
2,2′–bipyridine	114 ± 6
$MnCl_2$	110 ± 5
$Mn(NO_3)_2$	133 ± 7
$Mn(OAc)_2$	117 ± 10
$Mn(SO_4)$	98 ± 9
[Mn(fum)] (**1**)	98 ± 10
$[Mn(fum)(bipy)(H_2O)]_n$ (**2**)	115 ± 6
[Mn(fum)(phen)] (**3**)	31 ± 2
$[Mn(phen)_2(H_2O)_2](fum)\cdot 4H_2O$ (**4**)	33 ± 2

[a] The compounds were tested at concentrations of 10 μg cm^{-3} of aqueous RPMI medium. Complexes **1**–**4** were insoluble in water and were used as suspensions. Yeast cells were grown for 24 h at 37°C. Results are presented as % cell growth and the effectiveness of the compounds is compared to the growth of the control (no compound added).

possibly results from the extensive hydrogen bonding that exists between the carboxylate oxygens and both the coordinated and uncoordinated water molecules within the crystal. The room temperature magnetic moments of powdered samples of complexes **1**, **2**, **3** and **4** (5.65, 5.89, 5.99 and 5.76 BM respectively) were in the range expected for manganese complexes where there is no significant exchange interaction between metal centres [15].

The fumarate complexes, the metal-free ligands and a number of simple manganese salts were each tested for their ability to inhibit the growth of *Candida albicans* (Table 5). Fumaric acid exhibits negligible fungitoxic activity. The simple manganese(II) salts are essentially inactive also. The fumarate complex **1** does not show fungistatic activity at all against the *Candida*. Both the uncoordinated 2,2′-bipyridine and its fumarate derivative (complex **2**) are also ineffective against the pathogen. However, the phenanthroline complexes **3** and **4** both exhibit discrete anti-*Candida* activity causing 69 and 67% inhibition of cell growth respectively. Significantly the 'metal free' 1,10-phenanthroline itself shows the greatest activity causing 77% inhibition of cell growth. However, we believe that the so-called metal-free 1,10-phenanthroline is probably coordinating to metal ions (other than the manganese) that are present in trace amounts in the growth medium and that it is these resulting metal–phenanthroline complexes that are responsible for the high anti-*Candida* activity. Studies are currently underway in our laboratories to examine this theory.

In conclusion, it would appear that fumaric acid whether coordinated or uncoordinated to manganese does not possess any anti-*Candida* properties. Furthermore, the presence of the NN-donor 2,2′-bipyridine does not improve the activity of the complex. The 1,10-phenanthroline molecule is a potent anti-*Candida* agent and upon reaction with the manganese fumarate yields complexes with comparable fungitoxic activity.

3. Experimental

Chemicals were purchased from commercial sources and used without further purification. IR spectra were recorded in the region 4000–400 cm^{-1} on a Nicolet-400 Impact spectrometer. Magnetic susceptibility measurements were made using a Johnson Matthey magnetic susceptibility balance. $[HgCo(SCN)_4]$ was used as a reference. Conductivity readings were obtained using a Ciba Corning model check-mate 90 conductivity meter. Satisfactory microanalytical data for the complexes were reported by the Microanalytical Laboratory, University College Cork, Ireland.

3.1. {Mn(fum)}$_n$ (**1**)

To a solution of fumH$_2$ (3.15 g, 27.14 mmol) in ethanol (100 cm^3) was added manganese(II) acetate (5.94 g, 24.44 mmol), and the reaction mixture was refluxed for 2 h. The product formed as a colourless solid. The reaction mixture was allowed to cool to room temperature and then the product was filtered. The material was washed with two portions of ethanol and then dried in air. Yield 3.72 g (90.06%). Complex **1** was sparingly soluble in warm EtOH and MeOH, and insoluble in distilled H$_2$O, acetone, ether and chloroform. *Anal*. Found: C, 28.20; H, 1.31. Calc.: C, 28.43; H, 1.19%. IR: 3449.25, 3086.57, 2361.19, 1575.37, 1467.91, 1387.31, 1199.25, 991.04, 809.70, 688.81, 594.78 cm^{-1}. $\mu_{eff}=5.65$ BM. $\Lambda_M(EtOH)=0.43$ S cm^2 mol^{-1}.

3.2. [Mn(fum)(bipy)(H$_2$O)]$_n$ (**2**)

Complex **1** (0.5 g, 2.96 mmol) and 2,2′-bipyridine (1.25 g, 8.00 mmol) were stirred in deionised water (100 cm^3) for 4 h to give a pale green solution. On standing for several days at room temperature the product formed as yellow crystals. The crystals were filtered off, washed with deionised water and ethanol and then air dried. Yield 0.77 g (84.05%). Complex **2** was sparingly soluble in warm distilled H$_2$O, and insoluble in EtOH, MeOH, acetone, ether and chloroform. *Anal*. Found: C, 48.75; H, 3.42; N, 8.14. Calc.: C, 48.99; H, 3.52; N, 8.16%. IR: 3415.67, 3106.7, 3079.85, 1689.55, 1608.86, 1588.81, 1555.22, 1494.21, 1474.63, 1441.04, 1387.31, 1320.15,1246.27, 1219.40, 1158.96, 1105.22, 1058.21, 1004.48, 977.61, 802.99, 762.69, 735.82, 682.09, 647.76, 628.36, 561.19, 486.53 cm^{-1}. $\mu_{eff}=5.89$ BM. $\Lambda_M(H_2O)=163$ S cm^2 mol^{-1}.

3.3. [Mn$_2$(fum)$_2$(phen)$_{2.5}$]·3H$_2$O (**3**) and [Mn(phen)$_2$(H$_2$O)$_2$](fum)·4H$_2$O (**4**)

Complex **1** (1.00 g, 5.92 mmol) and 1,10-phenanthroline (2.12 g, 10.69 mmol) were refluxed in ethanol (150 cm^3) for 2 h. Upon cooling to room temperature the resulting yellow suspension was filtered to give a yellow powder and a yellow filtrate. The yellow product (**3**) was washed with ethanol and then air dried. Yield 1.86 g (37.29%). Complex **3** was sparingly soluble in warm MeOH and chloroform, and insoluble in distilled H$_2$O, EtOH, acetone and ether. *Anal*. Found: C, 54.23; H, 3.31; N, 8.63. Calc.: C, 54.17; H, 3.59; N, 8.31%. IR: 3449.13, 1602.24, 1514.93, 1420.90, 1205.97, 1151.60, 1105.22, 991.04, 970.22, 843.28, 809.70, 775.40, 729.10, 675.37, 634.32 cm^{-1}. $\mu_{eff}=5.76$ BM. $\Lambda_M(MeOH)=1.52$ S cm^2 mol^{-1}.

Upon standing at room temperature for 7 months yellow crystals of complex **4** precipitated from the filtrate. The crystals were filtered, washed with acetone and then dried in air. Yield 0.27 g (0.07%). Complex **4** was sparingly soluble in warm MeOH and insoluble in distilled H$_2$O, EtOH, acetone, chloroform and ether. *Anal*. Found: C, 56.35; H, 4.02; N, 9.67. Calc.: C, 52.75; H; 4.74; N, 8.79%. IR: 3388.81, 1575.37, 1514.93, 1427.61, 1360.45, 1212.69, 1089.51, 850.00 cm $^{-1}$. $\mu_{eff}=$ 5.99 BM. $\Lambda_M(MeOH)=0$ S cm^2 mol^{-1}.

3.4. X-ray crystallography

Crystal data for $[Mn(fum)(bipy)(H_2O)]_n$ (**2**) and $[Mn(phen)_2(H_2O)_2](fum)\cdot 4H_2O$ (**4**) are summarised in Table 6. Data sets for both complexes were collected using a Siemens SMART CCD diffractometer and were corrected for Lorentz, polarisation and absorption effects. The structures were solved by direct methods [16] and refined by full-matrix least-squares on F^2 using all the data. All the non-hydrogen atoms were refined with anistropic atomic displacement, hydrogen atoms were inserted at calculated positions with their isotropic displacement parameters riding on U_{ij} of their carrier atoms (except for those on the water molecules which were located from difference Fourier maps and their positions either allowed to refine (for complex **2**) or were not further refined (for complex **4**)). The programmes used in the final structure refinement are contained in the SHELXL-97 package [17].

3.5. Anti-Candida susceptibility testing

Candida albicans isolate was obtained commercially from Oxid Culti-loops (ATCC 10231). The isolate was stored on Sabouraud dextrose agar (SDA) plates at 4°C.

Suspensions of the test complexes were prepared by grinding them to a fine powder (0.02 g) followed by addition to sterile distilled water (100 cm^3). This process yielded stock suspensions of 200 μg cm^{-3}. These suspensions were furthered diluted to 100 μg cm^{-3}.

RPMI-1640 broth medium (Sigma R 7755) was used for the anti-*Candida* susceptibility testing. The medium (1 dm^3) was supplemented with L-glutamine (0.3 g) and morpholinepropanesulfonic acid (MOPS) (34.6 g) and was then adjusted to pH 7.0 using sterile NaOH (0.2 M). The broth microdilution reference method was used, NCCLS publication M27-P [18]. Prior to testing, yeast cells were grown on Sabouraud dextrose agar (SDA) at 37°C for 24 h. Cell suspensions were prepared in sterile phosphate buffered saline (5 cm^3) to a density of 1 McFarland standard. A 1:100 dilution of these cell suspensions were made in RPMI-1640 medium so that the cell concentration of the final inoculum was 3.5×10^4–5.0×10^5 cells cm^{-3}. The prepared cell sus-

Table 6
Summary of crystal data, data collection, structure solution and refinement details for complexes **2** and **4**

	2	**4**
Complex	$[Mn(fum)(bipy)(H_2O)]$	$[Mn(Phen)_2(H_2O)_2](fum)\cdot 4H_2O$
Formula	$C_{14}H_{12}MnN_2O_5$	$C_{28}H_{30}MnN_4O_{10}$
Description	pale yellow block	pale yellow block
Crystal size (mm)	0.24×0.45×0.6	0.52×0.50×0.28
Temperature (K)	158(2)	164(2)
a (Å)	9.105(3)	10.6034(17)
b (Å)	15.057(4)	10.6499(17)
c (Å)	19.814(5)	13.565(2)
α (°)	90	96.122(2)
β (°)	90	94.658(3)
γ (°)	90	105.002(2)
U (Å^{-3})	2879(1)	1461(4)
$F(000)$	1400	662
Crystal system	orthorhombic	triclinic
Space group	$Pbca$	$P\bar{1}$
Z	8	2
Density calc. (Mg m^{-3})	1.584	1.448
μ (mm^{-1})	0.942	0.515
T_{max}, T_{min}	1.00, 0.829	1.00, 0.860
θ Range (°)	2.06–26.49	2.00–26.35
Index ranges	$-11\leq h\leq 11$, $-19\leq k\leq 12$, $-24\leq l\leq 24$	$-11\leq h\leq 13$, $-13\leq k\leq 13$, $-8\leq l\leq 16$
Reflections collected	34298	11962
Independent reflections	2943	5861
R_{int}	0.0342	0.0160
Data/restraints/parameters	2943/0/205	5861/0/389
Goodness of fit on F^2	1.054	1.043
R_1, wR_2 ($I>2\sigma(I)$)	0.0277, 0.0751	0.0280, 0.0797
R_1, wR_2 (all data)	0.0351, 0.0767	0.0315, 0.0815

pension (900 μl) was dispensed into sterile test tubes and to this was added the test complex solutions (100 μl) to yield working solutions of the test complexes of concentration 10 μg cm^{-3}. The test tubes were then incubated in a shaking water bath for 24 h at 37°C with continuous shaking. Each complex was assessed in triplicate and three independent experiments were performed.

Supplementary data

Supplementary data for the three structures are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), on request quoting the deposition numbers CCDC 137687 and CCDC 137688, respectively.

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