

## Designer ligands. Part 15. Synthesis and characterisation of novel Mn(II), Ni(II) and Zn(II) complexes of 1,10-phenanthroline-derived ligands

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### Abstract

Series of manganese(II), nickel(II) and zinc(II) complexes have been prepared using 1,10-phenanthroline-derived ligands, and their coordination geometries have been assigned using infrared data. It is apparent that, depending on the ligand, the metal centres adopt octahedral, tetrahedral and distorted tetrahedral coordination geometries. The catecholase activity of the manganese(II) complexes has also been investigated.

**Keywords:** Manganese(II), nickel(II) and zinc(II) complexes, mononuclear, dinuclear, biomimetic, ligands, catecholase activity

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### Introduction

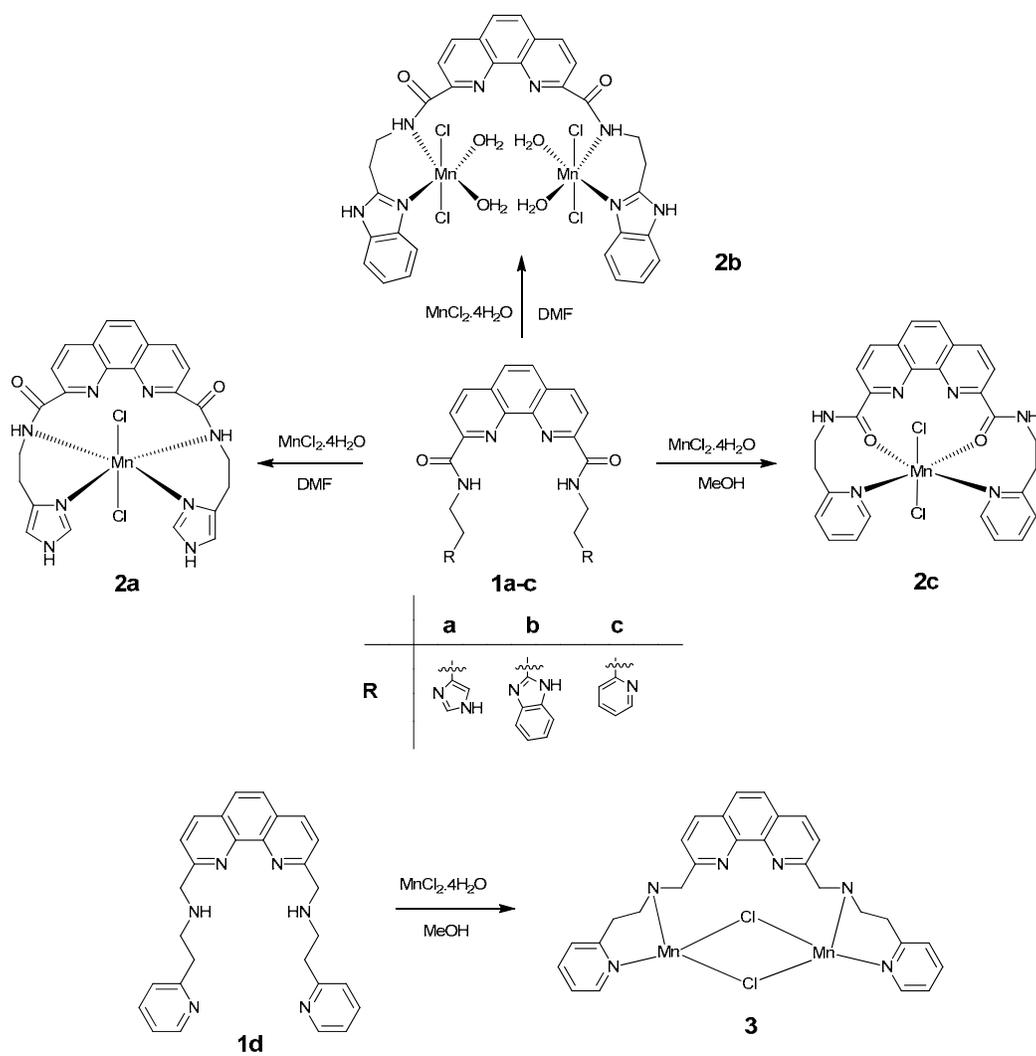
The complexation of appropriate metals is critical in the biological function of many enzymes and it has been shown that catalytic activity in several enzyme models is dependent on nuclearity; mononuclear complexes often appear to exhibit a decrease in, or absence of, catalytic activity in contrast to their dinuclear counterparts.<sup>1-4</sup> Mononuclear manganese centres have been found in the oxygen evolving center (OEC) of photosystem II (PS-II)<sup>5</sup> and in numerous enzymes,<sup>6</sup> including the superoxide dismutase, Mn-SOD,<sup>7</sup> and Mn-dioxygenase.<sup>8</sup> Dinuclear manganese centres, on the other hand, have been found in various metalloenzymes,<sup>14</sup> including catalase,<sup>9-11</sup> Mn-ribonucleotide reductase<sup>12</sup> and arginase.<sup>13</sup> Nickel has been found in ureases,<sup>15</sup> hydrogenases, CO dehydrogenases and coenzyme F<sub>430</sub>.<sup>16</sup> Hydrogenases occur in many bacteria where they are responsible for catalyzing the oxidation of molecular hydrogen, while CO dehydrogenase interconverts carbon monoxide and carbon dioxide. Hydrogenases and CO dehydrogenases have nickel(III) (low spin  $d^7$ ) as well as Fe-S clusters present in their structures.<sup>16</sup> Nickel(II) exists in a square planar geometry in Coenzyme F<sub>430</sub> which is a cofactor

of methyl coenzyme M reductase. Zinc is found in many enzymes, exhibiting active catalytic or structural roles. Zinc-containing enzymes include carbonic anhydrase, carboxypeptidase, alcohol dehydrogenase, thermolysin and  $\beta$ -lactamase.<sup>17-20</sup>

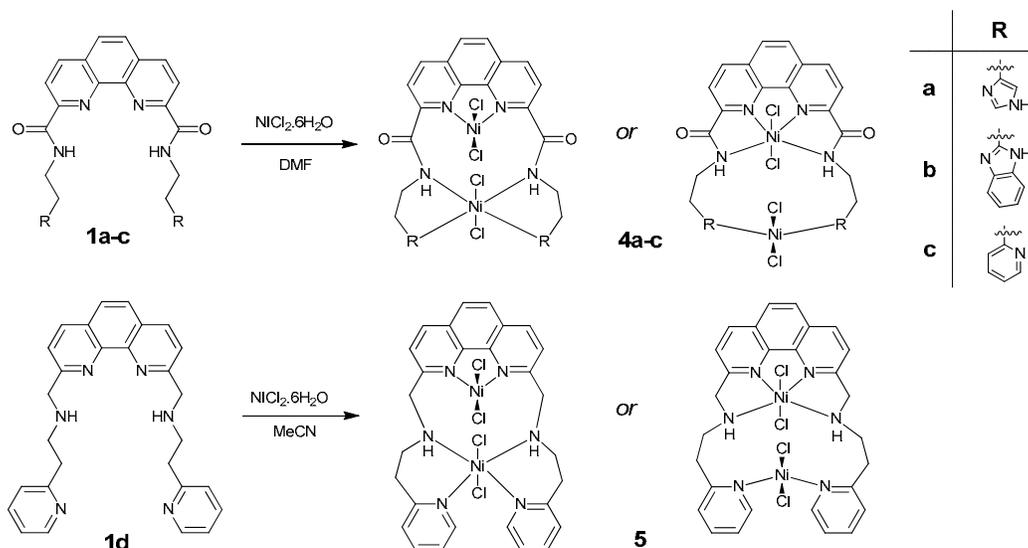
We have previously described the preparation of ligands which are capable of chelating two metal ions and in which the coordinating moieties are separated by biphenyl<sup>21</sup> and 1,10-phenanthroline<sup>22</sup> and, more recently, the preparation of manganese(II), nickel(II) and zinc(II) complexes using various benzamide- and biphenyl-derived ligands.<sup>23</sup> In this paper, we now report:- the synthesis and structural assignment of three series of novel Mn(II), Ni(II) and Zn(II) complexes of 1,10-phenanthroline-derived multidentate ligands containing amido, amino and heterocyclic moieties, and the catecholase activity of the manganese(II) complexes.

## Results and Discussion

The synthesis of the 1,10-phenanthroline-derived ligands **1a-d** has been reported previously,<sup>24</sup> and Schemes 1-3 outline the use of these ligands in the formation of the corresponding Mn(II), Ni(II) and Zn(II) complexes. The structural assignments are based on a consideration of the microanalysis and infrared data and, in the case of the Zn(II) complexes **6b,c** and **7** (Scheme 3), on the <sup>1</sup>H- and <sup>13</sup>C-NMR data.



**Scheme 1.** Manganese(II) complexes of the 1,10-phenanthroline-derived ligands **1a-d**.



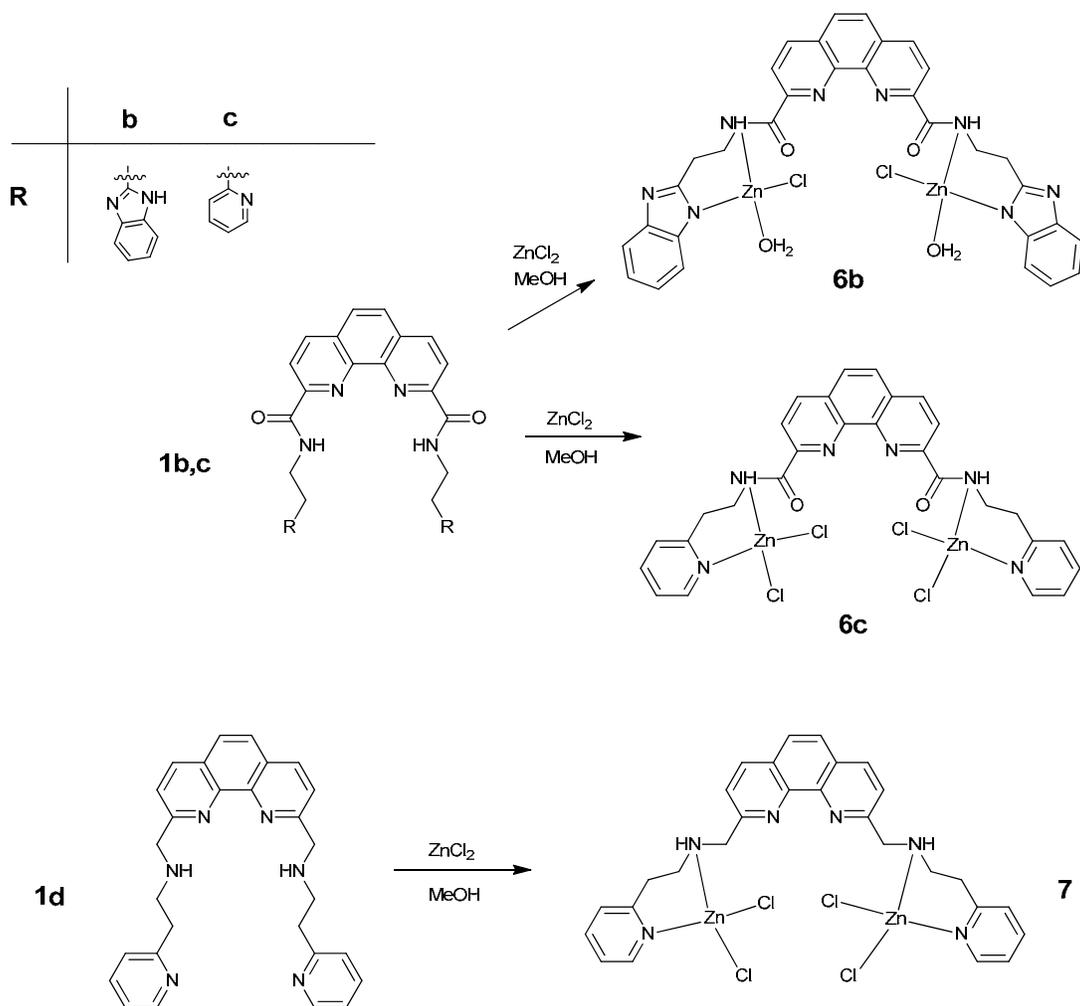
**Scheme 2.** Nickel(II) complexes of the 1,10-phenanthroline-derived ligands **1a-d**.

Microanalysis data for the various complexes are summarized in Table 1. It is apparent that complexes **2a** and **2c** are mononuclear while complexes **2b** and **3** are dinuclear. All of the Mn complexes contain two chloride ions except complex **2b**, which contains four (Scheme 1). The nickel complexes **4a-c** and **5** all appear to be dinuclear and each complex contains four chloride ions (Scheme 2). Similarly, the zinc complexes **6b,c** and **7** also all appear to be dinuclear and each complex contains four chloride ions except complex **6b** which contains two (Scheme 3).

**Table 1.** Microanalytical data for the manganese(II), nickel(II) and zinc(II) complexes followed, in parentheses, by the calculated values

Complex	Complex Stoichiometry <sup>a</sup>	% Carbon	% Hydrogen	% Nitrogen
<b>2a</b>	Mn( <b>1a</b> )Cl <sub>2</sub> ·6H <sub>2</sub> O	42.6 (41.9)	4.7 (5.0)	16.0 (16.3)
<b>2b</b>	Mn <sub>2</sub> ( <b>1b</b> )Cl <sub>4</sub> ·6½H <sub>2</sub> O	41.7 (41.6)	4.2 (4.3)	11.8 (12.1)
<b>2c</b>	Mn( <b>1c</b> )Cl <sub>2</sub> ·6H <sub>2</sub> O	47.3 (47.3)	4.7 (5.1)	11.8 (12.2)
<b>3</b>	Mn <sub>2</sub> ( <b>1d</b> )Cl <sub>2</sub> ·3½H <sub>2</sub> O	49.2 (48.7)	4.4 (4.8)	11.8 (12.2)
<b>4a</b>	Ni <sub>2</sub> ( <b>1a</b> )Cl <sub>4</sub> ·2½H <sub>2</sub> O	42.6 (43.1)	4.0 (3.8)	11.3 (10.8)
<b>4b</b>	Ni <sub>2</sub> ( <b>1b</b> )Cl <sub>4</sub> ·7H <sub>2</sub> O	40.7 (40.9)	3.8 (4.3)	12.8 (11.9)
<b>4c</b>	Ni <sub>2</sub> ( <b>1c</b> )Cl <sub>4</sub> ·2H <sub>2</sub> O	37.6 (38.5)	4.2 (3.5)	14.5 (15.0)
<b>5</b>	Ni <sub>2</sub> ( <b>1d</b> )Cl <sub>4</sub> ·3H <sub>2</sub> O	44.1 (44.2)	4.0 (4.5)	11.0 (11.0)
<b>6b</b>	Zn <sub>2</sub> ( <b>1b</b> )Cl <sub>2</sub> ·3H <sub>2</sub> O	51.8 (51.6)	4.0 (3.5)	15.2 (15.0)
<b>6c</b>	Zn <sub>2</sub> ( <b>1c</b> )Cl <sub>4</sub> ·½H <sub>2</sub> O	44.8 (44.4)	3.4 (3.3)	11.3 (11.1)
<b>7</b>	Zn <sub>2</sub> ( <b>1d</b> )Cl <sub>4</sub> ·2H <sub>2</sub> O	44.9 (44.4)	3.5 (4.3)	10.6 (11.1)

<sup>a</sup> Presence of H<sub>2</sub>O supported by IR data; see Table 2 for  $\nu(\text{OH}_2)$  data.



**Scheme 3.** Zinc(II) complexes of the 1,10-phenanthroline-derived ligands **1b-d**.

The orientation of the chloride atoms within the coordination sphere(s) in each complex was deduced from the far-IR spectroscopic data. The mid-IR data provided a basis for determining whether the metal ions coordinate through the amide nitrogen or oxygen atoms, a negative shift for the amide carbonyl band (amide I) indicating coordination *via* the amide oxygen, a positive shift coordination *via* the amide nitrogen. The relevant mid- and far-IR data for all of the complexes examined are summarised in Table 2.

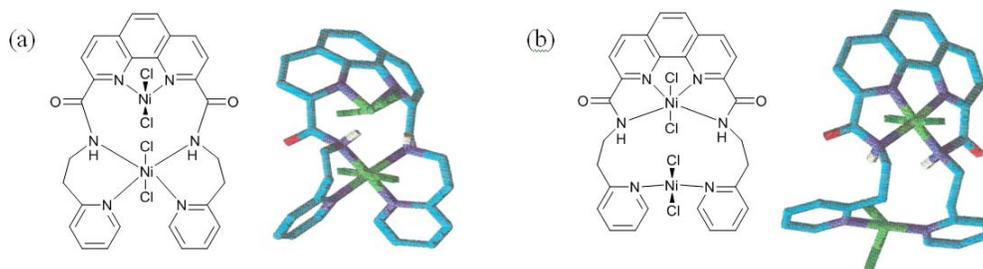
**Table 2.** Summary of the IR frequencies ( $\nu_{\text{M-Cl}}$ ) and the amide frequency shifts ( $\Delta\nu_{\text{NH}}$  and  $\Delta\nu_{\text{C=O}}$ ) on formation of the metal complexes, together with residual water bands

Complex	$\Delta\nu_{\text{NH}}/\text{cm}^{-1}$	$\Delta\nu_{\text{C=O}}/\text{cm}^{-1}$	$\nu_{\text{M-Cl}}/\text{cm}^{-1}$	$\nu_{\text{OH}}/\text{cm}^{-1}$
<b>2a</b>	-27	4	245	3400
<b>2b</b>	-71	16	270	3400 (sh)
<b>2c</b>	-27	-4	277	3366
<b>3</b>			220, 281	3392
<b>4a</b>	-33	2	310, 373	3398
<b>4b</b>	-78	23	283, 384	3400
<b>4c</b>	-61	0	253, 378	3359
<b>5</b>			278, 352	3367
<b>6b</b>	43	27	283, 313	3366
<b>6c</b>	34	2	304	3460 (sh)
<b>7</b>			302	3481

For the mononuclear Mn(II) complex **2a**, a positive shift of the amide carbonyl band and the negative shift of the amide NH band (relative to the free ligand) indicate coordination through the amide nitrogens, while a band at  $3137\text{ cm}^{-1}$ , assigned to the imidazole NH stretch, suggests coordination with the imidazole tertiary nitrogen atoms. The microanalysis data suggest the presence of two chloride anions in this mononuclear complex, supporting the assumption that the amide protons were not removed on formation of the complex. In the case of the dinuclear Mn(II) complex **2b**, an amide NH band also appears to be present, although the benzimidazole NH band is believed to be masked by water; the presence of four chloride atoms suggest that the benzimidazole moieties have not been deprotonated. The positive shift of the amide carbonyl band and the negative shift of the amide NH band again indicate coordination through the amide nitrogens. The negative shifts observed for the amide carbonyl and NH bands of the mononuclear Mn(II) complex **2c**, on the other hand, indicate coordination through the amide oxygen. The secondary amine NH band could not be seen in the spectrum of the Mn(II) complex **3** and deprotonation is supported by the presence of only two chloride anions for this dinuclear complex. The bands at 245, 270 and  $277\text{ cm}^{-1}$  in the far-IR spectra of complexes **2a-c** indicate apical octahedral orientations of the chloride ligands,<sup>25</sup> while the two bands observed at 281 and  $220\text{ cm}^{-1}$  for complex **3** is characteristic of chloride bridging.<sup>26</sup>

The Ni(II) complexes **4a-c** all exhibit negative shifts of the amide NH band indicating coordination through the amide nitrogens – a conclusion supported by the positive amide C=O band shifts in complexes **4a,b**; the microanalysis data also provide evidence for the presence of four chloride ligands in these complexes. The strong bands in the region  $370\text{-}390\text{ cm}^{-1}$  for complexes **4a-c** are attributed to *trans*-coordinated chloride ions in an octahedral environment, while others at 253, 283 and  $310\text{ cm}^{-1}$ , are indicative of chloride ions coordinated in a tetrahedral environment.<sup>27,28</sup> Similar bands are evident for complex **5** at 278 and  $352\text{ cm}^{-1}$ , but the location of the respective metal centres within all four Ni(II) complexes is not clear (as indicated in Scheme 2). Interestingly, the structure of the microbial urease from *Klebsiella aerogenes*

contains pseudotetrahedrally coordinated nickel,<sup>29</sup> while Meyer has reported ethanolsysis of urea by an asymmetrical dinuclear nickel complex containing one nickel atom having octahedral and the other trigonal bipyramidal geometry.<sup>30</sup> In the absence of X-ray crystal structures, computer modelling at the Molecular Mechanics level was used to explore the possible 3-D structures of the dinuclear nickel complexes. For complex **4c**, for example, it seems that isomer (a) is the favored structure. In both cases, one of the nickel(II) ions is octahedral and the other distorted tetrahedral.

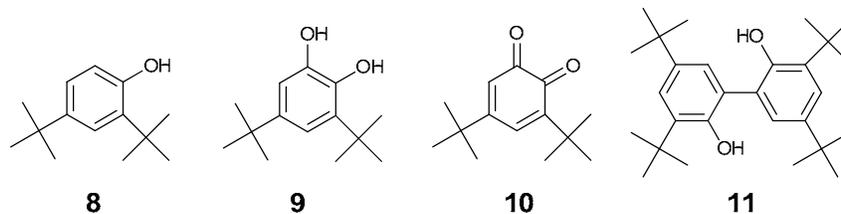


**Figure 1.** Computer-modelled structures of isomeric possibilities for the nickel(II) complex **4c**.

The positive shifts observed for the amide carbonyl bands in complexes **6b,c** are also indicative of coordination through the amide nitrogens, although the amide NH shifts are positive in both cases. The benzimidazole NH band for complex **6b** also cannot be seen but the microanalysis data indicate the presence of only two chloride atoms and, hence, that deprotonation of the benzimidazole moiety had, in fact, occurred. An IR band at  $3237\text{ cm}^{-1}$  for complex **7** suggests that complexation does not require deprotonation of the secondary amine, a shift of  $120\text{ cm}^{-1}$  for this NH band (relative to the free ligand) reflecting coordination with the aliphatic amine nitrogen. Two Zn-Cl bands ( $283$  and  $313\text{ cm}^{-1}$ ) characteristic of tetrahedral coordination geometry for zinc are observed for complex **6b**,<sup>27</sup> but comparable bands are not observed for the other Zn(II) complexes. Instead, a very strong, broad band, with a lower and higher frequency shoulder, is observed at *ca.*  $300\text{ cm}^{-1}$  for complexes **6c** and **7**, respectively. This may be due to accidental degeneracy of the symmetric and anti-symmetric Zn-Cl stretches and is indicative of distorted tetrahedral zinc arrangements within these complexes.

Dinuclear copper(II) complexes are the most reported functional mimics of catechol oxidase, but catalytically active complexes containing other transition metal ions such as Mn, Co or Ni<sup>31,32</sup> are also known. As part of our research on the development of complexes that mimic the active site of the enzyme tyrosinase,<sup>33</sup> we also explored the phenolase and catecholase activity of the Mn(II) complexes **2a-c** and **3**. For a model to successfully mimic the enzyme tyrosinase it must be capable of oxidizing a phenol and/or catechol. For this study, 3,5-di-*t*-butylphenol (3,5-DTBP) **8** and 3,5-di-*t*-butylcatechol (3,5-DTBC) **9** were selected as substrates since they are activated by their alkyl substituents and are somewhat resistant to polymerization.<sup>34-36</sup> 3,5-DTBP **8** is oxidized to 3,5-DTBC **9** (phenolase activity) which is subsequently oxidized to 3,5-DTBQ

**10** (catecholase activity). DTBP **8** can also be oxidized to the coupled product **11**. These reactions were conducted in DMF in the presence of triethylamine (Et<sub>3</sub>N) and the oxidation product(s) were detected using <sup>1</sup>H NMR spectroscopy.



**Table 3.** Catalytic activity of the manganese complexes in the presence of Et<sub>3</sub>N

Complex	Solvent	Reaction Time/h	Phenolase Activity Product	Catecholase Activity Product	% Conversion Within 24 h	Recyclability % conversion within 24 h
<b>2a</b>	DMF	24	none	<i>o</i> -quinone	67	-
<b>2b</b>	DMF	24	none	<i>o</i> -quinone	100	100
<b>2c</b>	DMF	24	none	none	-	-
<b>3</b>	DMF	24	none	<i>o</i> -quinone	100	100

It is apparent from an examination of the data in Table 3 that none of the complexes exhibited phenolase activity. The *axial* binding of the phenol to the metal centre and Berry pseudorotation of the trigonal bipyramidal complex, required to expose the *equatorial* substrate to *ortho*-hydroxylation appears to be inhibited in all four cases. Catecholase activity only requires a transfer of electrons and is, in fact, observed for three of the complexes (**2a,b** and **3**), with the dinuclear complexes **2b** and **3** exhibiting higher conversion rates than the mononuclear complex **2a** and excellent re-cyclability. The conversion rates (Table 3) are higher than those observed previously for biphenyl dinuclear cobalt(II)<sup>37</sup> and macrocyclic dinuclear copper(I) and copper(II) complexes,<sup>38</sup> but similar to those exhibited by macrocyclic dinuclear cobalt(II),<sup>38</sup> mononuclear Mn(II) benzamide and dinuclear biphenyl Mn(II) manganese complexes.<sup>23</sup> Catalase, itself, has two manganese ions in its active site and catalyzes the disproportionation of two hydrogen peroxide molecules to two molecules of water and one of dioxygen, and the catalytic activity of complexes **2b** and **3** may be attributed to the fact that they are dinuclear and have similar structures to that of the complex reported by Dismukes.<sup>39</sup> The apparent inactivity of complex **2c** may be attributed to strong binding of the metal to the amide oxygens rather than the nitrogens and to the relative basicity of the pyridine nitrogen; without the presence of weakly coordinated H<sub>2</sub>O or amide NH, dissociation of the complex to form the necessary trigonal bipyramidal intermediate is not possible. The catalytic oxidation of 3,5-DTBC **9** to 3,5-DTBQ **10** by a series of mononuclear manganese complexes has been reported previously.<sup>40</sup>

## Conclusions

The 1,10-phenanthroline ligands **1a-d** clearly form complexes with manganese(II), nickel(II) and zinc(II) and, depending on the ligand, the metal centres in these complexes adopt octahedral, tetrahedral or distorted tetrahedral coordination geometries – patterns observed in our earlier communication.<sup>23</sup> Microanalytical, mid- and far-infrared and, where appropriate, NMR spectroscopic data have all been used to assign structures to the complexes and computer modelling has been used to explore structural preferences between isomeric possibilities. The manganese(II) complexes **2a**, **2b** and **3** have been shown to exhibit significant catecholase activity (67 – 100% conversion within 24 hours), while complexes **2b** and **3** also exhibit excellent recyclability.

## Experimental Section

**General.** Infrared spectra were recorded on a Perkin Elmer 2000 spectrophotometer using potassium bromide discs (4000-400  $\text{cm}^{-1}$ ) and nujol mulls (650-30  $\text{cm}^{-1}$ ). NMR spectra were recorded on a Bruker AMX 400 spectrometer and chemical shifts are reported relative to the solvent signals. Melting points were obtained using a hot-stage microscope and are uncorrected. Microanalysis (combustion analysis) was conducted at the University of Cape Town. Exploratory modelling of selected ligands and complexes was undertaken using the MSI Cerius2 platform on a Silicon Graphics O<sub>2</sub> computer.<sup>41</sup>

**The manganese complex 2a.** A solution of 2,9-bis{[2-(4-imidazolyl)ethylamino]carbonyl}-1,10-phenanthroline **1a** (0.20 g, 0.64 mmol) in hot DMF (3 mL) was added to a stirred solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.26 g, 1.3 mmol) in DMF (2 mL). After stirring for 20 h at room temperature,  $\text{Et}_2\text{O}$  was added to precipitate the product as a yellow powder (0.28 g, 64%). Recrystallisation from DMSO-DMF-EtOAc yielded the *manganese complex 2a* (0.13 g, 30%), m.p. 231-233°C;  $\nu_{\text{max}}(\text{KBr}/\text{cm}^{-1})$  3400 vs br sh (water OH), 3270 vs br (amide NH), 3137 vs (imidazole NH) and 1653 vs (CO);  $\nu_{\text{max}}(\text{nujol}/\text{cm}^{-1})$  245 m (Mn-Cl).

**The manganese complex 2b.** A solution of 2,9-bis{[2-(2-benzimidazolyl)ethylamino]carbonyl}-1,10-phenanthroline **1b** (0.20 g, 0.36 mmol) in DMF (3 mL) was added dropwise to a solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.14 g, 0.72 mmol) in DMF (2 mL). The resulting mixture was stirred for 44.5 h, followed by the addition of  $\text{Et}_2\text{O}$  which resulted in the precipitation of the product. Recrystallisation from DMF- $\text{Et}_2\text{O}$  yielded, as a yellow powder, the *manganese complex 2b* (0.20 g, 60%), m.p. >250°C;  $\nu_{\text{max}}(\text{KBr}/\text{cm}^{-1})$  3400 s br sh (water OH), 3252 vs br (amide NH) and 1646 vs (CO);  $\nu_{\text{max}}(\text{nujol}/\text{cm}^{-1})$  270 mw (Mn-Cl).

**The manganese complex 2c.** A solution of 2,9-bis{[2-(2-pyridyl)ethylamino]carbonyl}-1,10-phenanthroline **1c** (0.17 g, 0.38 mmol) in MeOH (5 mL) was added dropwise to a hot, stirred solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.15 g, 0.76 mmol) in MeOH (3 mL). Stirring was continued for 48 h

before adding Et<sub>2</sub>O to precipitate the product. Recrystallisation from MeOH-Et<sub>2</sub>O afforded, as a yellow powder, the *manganese complex 2c* (0.13 g, 48%), m.p. 174-176°C;  $\nu_{\max}$ (KBr/cm<sup>-1</sup>) 3366 vs br (water OH), 3229 vs br (amide NH) and 1647 vs (CO);  $\nu_{\max}$ (nujol/cm<sup>-1</sup>) 277 m (Mn-Cl).

**The manganese complex 3.** A solution of 2,9-bis{[2-(2-pyridyl)ethylamino]methyl}-1,10-phenanthroline **1d** (0.20 g, 0.44 mmol) in MeOH (3 mL) was added dropwise to a solution of MnCl<sub>2</sub>·4H<sub>2</sub>O (0.17 g, 0.88 mmol) in MeOH (3 mL). After stirring for 48 h, Et<sub>2</sub>O was added to precipitate the product as a brown powder (0.16 g, 53%). Recrystallisation from DMF-Et<sub>2</sub>O afforded, as a brown powder, the *manganese complex 3* (0.14 g, 46%), m.p. 197-199°C;  $\nu_{\max}$ (KBr/cm<sup>-1</sup>) 3392 vs br (water OH);  $\nu_{\max}$ (nujol/cm<sup>-1</sup>) 281 m and 220 m (Mn-Cl).

**The nickel complex 4a.** A solution of 2,9-bis{[2-(4-imidazolyl)ethylamino]carbonyl}-1,10-phenanthroline **1a** (0.20 g, 0.44 mmol) in DMF (6.5 mL) was added dropwise to a stirred solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.21 g, 0.88 mmol) in DMF (5 mL). The resulting suspension was stirred for 20.5 h before adding Et<sub>2</sub>O to precipitate, as a light-green solid, the *nickel complex 4a* (0.31 g, 94%), m.p. >250°C;  $\nu_{\max}$  (KBr/cm<sup>-1</sup>) 3398 vs br (water OH), 3236 vs sh (amide NH) and 1649 vs (CO);  $\nu_{\max}$ (nujol/cm<sup>-1</sup>) 373 m and 310 w (Ni-Cl).

**The nickel complex 4b.** A solution of 2,9-bis{[2-(2-benzimidazolyl)ethylamino]carbonyl}-1,10-phenanthroline **1b** (0.22 g, 0.44 mmol) in DMF (15 mL) was added dropwise to a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.20 g, 0.92 mmol) in DMF (7 mL). After stirring for 52 h, Et<sub>2</sub>O was added to precipitate, as a brown, hygroscopic solid, the *nickel complex 4b* (0.31 g, 66%), m.p. >250°C;  $\nu_{\max}$  (KBr/cm<sup>-1</sup>) 3650 vs br (water OH), 3245 vs sh (amide NH) and 1653 vs (CO);  $\nu_{\max}$ (nujol/cm<sup>-1</sup>) 384 m and 283 w (Ni-Cl).

**The nickel complex 4c.** To a stirred solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.20 g, 0.92 mmol) in MeOH (5 mL), a solution of 2,9-bis{[2-(2-pyridyl)ethylamino]carbonyl}-1,10-phenanthroline **1c** (0.20 g, 0.44 mmol) in DMF (5 mL) was added dropwise. Although no immediate color change was observed, a suspension formed during stirring for 48 h. Et<sub>2</sub>O was then added to the reaction mixture to precipitate, as a light-green solid, the *nickel complex 4c* (0.24 g, 71%), m.p. 249-252°C;  $\nu_{\max}$  (KBr/cm<sup>-1</sup>) 3359 vs br (water OH), 3228 vs sh (amide NH) and 1653 vs (CO);  $\nu_{\max}$  (nujol/cm<sup>-1</sup>) 378 m and 253 w (Ni-Cl).

**The nickel complex 5.** A solution of 2,9-bis{[2-(2-pyridylethylamino)methyl]-1,10-phenanthroline **1d** (0.25 g, 0.56 mmol) in MeOH (5 mL) was added dropwise to a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.26 g, 1.11 mmol) in MeOH (5 mL). The color changed from light-green to dark-green and, after stirring for 48 h, Et<sub>2</sub>O was added to precipitate, as a light-green solid, the *nickel complex 5* (0.30 g, 70%), m.p. 244-246°C;  $\nu_{\max}$  (KBr/cm<sup>-1</sup>) 3367 vs br (NH);  $\nu_{\max}$  (nujol/cm<sup>-1</sup>) 352 w and 278 w (Ni-Cl).

**The zinc complex 6b.** A solution of 2,9-bis{[2-(2-benzimidazolyl)ethylamino]carbonyl}-1,10-phenanthroline **1b** (0.20 g, 0.36 mmol) in DMF (3 mL) was added dropwise to a solution of ZnCl<sub>2</sub> (0.10 g, 0.72 mmol) in MeOH (5 mL). The resulting mixture was stirred for 43 h, during which time the colour changed from purple-blue to dark-green. The volume of the reaction mixture was reduced to less than half by evaporating off the solvent under reduced pressure. The subsequent addition of Et<sub>2</sub>O resulted in the precipitation of a light-brown powder (0.25 g, 93%).

Recrystallisation from DMF-Et<sub>2</sub>O afforded the *zinc complex 6b* (0.13 g, 48%), m.p. >250°C;  $\nu_{\max}(\text{KBr}/\text{cm}^{-1})$  3366 s br (water OH), 3252 s br (amide NH) and 1657 vs (CO);  $\nu_{\max}(\text{nujol}/\text{cm}^{-1})$  313 m and 283 m (Zn-Cl);  $\delta_{\text{H}}(400 \text{ MHz}; \text{DMSO}-d_6)$  3.55 (4H, br s, CH<sub>2</sub>CH<sub>2</sub>N), 3.96 (4H, br s, CH<sub>2</sub>CH<sub>2</sub>N), 7.21 (4H, br s, ArH), 7.68 (4H, br s, ArH), 8.14 (2H, br s, ArH), 8.44 (2H, br s, ArH), 8.70 (2H, br s, ArH), 9.48 (2H, br s, ArH) and 13.2 (2H, v. br s, NH);  $\delta_{\text{C}}(100 \text{ MHz}; \text{DMSO}-d_6)$  28.3 (t, CH<sub>2</sub>), 37.4 (t, CH<sub>2</sub>N), 120.8 (d), 122.5 (d), 127.7 (d), 130.1 (s), 138.1 (d), 143.4 (s), 149.2 (s), 154.1 (s), 162.2 (d) and 163.9 (s, C=O).

**The zinc complex 6c.** A solution of 2,9-bis{[2-(2-pyridyl)ethylamino]carbonyl}-1,10-phenanthroline **1c** (0.17 g, 0.38 mmol) in MeOH (3 mL) was added dropwise to a hot, stirred solution of ZnCl<sub>2</sub> (0.10 g, 0.76 mmol) in MeOH (4 mL). Stirring was continued for 24 h before adding Et<sub>2</sub>O to precipitate, as a light-brown solid, the *zinc complex 6c* (0.16 g, 56%), m.p. 220-222°C;  $\nu_{\max}(\text{KBr}/\text{cm}^{-1})$  3460 s sh (water OH), 3290 s (NH) and 1653 vs (CO);  $\nu_{\max}(\text{nujol}/\text{cm}^{-1})$  304 w m and 280 w m sh (Zn-Cl);  $\delta_{\text{H}}(400 \text{ MHz}; \text{DMSO}-d_6)$  3.18 (4H, br s, CH<sub>2</sub>CH<sub>2</sub>N), 3.81 (4H, br s, CH<sub>2</sub>CH<sub>2</sub>N), 7.20 (2H, t, ArH), 7.35 (2H, d, ArH), 7.68 (2H, t, ArH), 8.18 (2H, br s, ArH), 8.48 (4H, br s, ArH), 8.76 (2H, br s, ArH) and 9.58 (2H, br s, NH);  $\delta_{\text{C}}(100 \text{ MHz}; \text{DMSO}-d_6)$  37.2 (t, CH<sub>2</sub>CH<sub>2</sub>N), 39.3 (t, CH<sub>2</sub>CH<sub>2</sub>N), 121.9 (d), 123.3 (d), 127.8 (d), 128.1 (d), 130.2 (s), 136.9 (d), 138.7 (s), 149.2 (d), 149.6 (s), 159.3 (s) and 164.0 (s, C=O).

**The zinc complex 7.** A solution of 2,9-bis{[2-(2-pyridyl)ethylamino]methyl}-1,10-phenanthroline **1d** (0.20 g, 0.44 mmol) in MeOH (3 mL) was added dropwise to a solution of ZnCl<sub>2</sub> (0.12 g, 0.88 mmol) in MeOH (5 mL). After stirring for 24 h, the *zinc complex 7* precipitated as a light-brown powder (0.24 g, 74%), decomposes >216°C;  $\nu_{\max}(\text{KBr}/\text{cm}^{-1})$  3481 vs br (water OH), 3237 s br (NH);  $\nu_{\max}(\text{nujol}/\text{cm}^{-1})$  315 sh, 302 m (Zn-Cl);  $\delta_{\text{H}}(400 \text{ MHz}; \text{DMSO}-d_6)$  3.20 (4H, br s, CH<sub>2</sub>CH<sub>2</sub>N), ca. 3.4 [4H, s (partially obscured by H<sub>2</sub>O signal), CH<sub>2</sub>CH<sub>2</sub>N], 4.50 (4H, br s, ArCH<sub>2</sub>N), 7.35 (2H, t, ArH), 7.46 (2H, d, ArH), 7.84 (2H, t, ArH), 8.13 (2H, d, ArH), 8.17 (2H, s, ArH), 8.41 (2H, d, ArH) and 8.82 (2H, d, ArH);  $\delta_{\text{C}}(100 \text{ MHz}; \text{DMSO}-d_6)$  36.7 (t, CH<sub>2</sub>CH<sub>2</sub>N), 49.9 (t, CH<sub>2</sub>CH<sub>2</sub>N), 53.4 (t, ArCH<sub>2</sub>N), 123.3 (d), 125.1 (d), 125.6 (d), 127.3 (d), 128.5 (s), 139.2 (d), 139.8 (s), 140.8 (d), 149.7 (d) and 160.7 (s).

### Biomimetic studies

The substrates DTBP and DTBC were added to solutions of the Mn(II) complexes in DMF, containing Et<sub>3</sub>N (see Table 3), to give substrate:complex molar ratios of 100:1. The resulting mixtures were aerated by stirring vigorously for 24h. At the conclusion of each reaction period, the mixture was concentrated to dryness *in vacuo* and the residue analysed by <sup>1</sup>H NMR spectroscopy to determine the substrate:product ratio. Recyclability was established by adding fresh substrate, DMF and Et<sub>3</sub>N to the residue from the initial reaction, and stirring for 24 h. The solvent was evaporated *in vacuo* and the residual material analyzed as before.

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