

## Designer ligands. Part 9.<sup>1</sup> Catalytic activity of biomimetic cobalt(II) and copper(II) complexes of multidentate ligands

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**Dedicated to Professor James R. Bull on his retirement**

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### Abstract

A series of Co(II) and Cu(II) complexes have been prepared, and their structures investigated using a combination of microanalytical, spectroscopic, electrochemical and X-ray crystallographic techniques. The capacity of the complexes to oxidise phenol and catechol substrates has been examined, and while some of the Cu(II) complexes catalyse oxidative coupling of 2,4-di-*t*-butylphenol (DTBP) to the corresponding biphenyl (9–13%), the Co(II) complexes catalyse efficient conversion (up to 92%) of 3,5-di-*t*-butylcatechol (DTBC) to the *o*-quinone within 24 h.

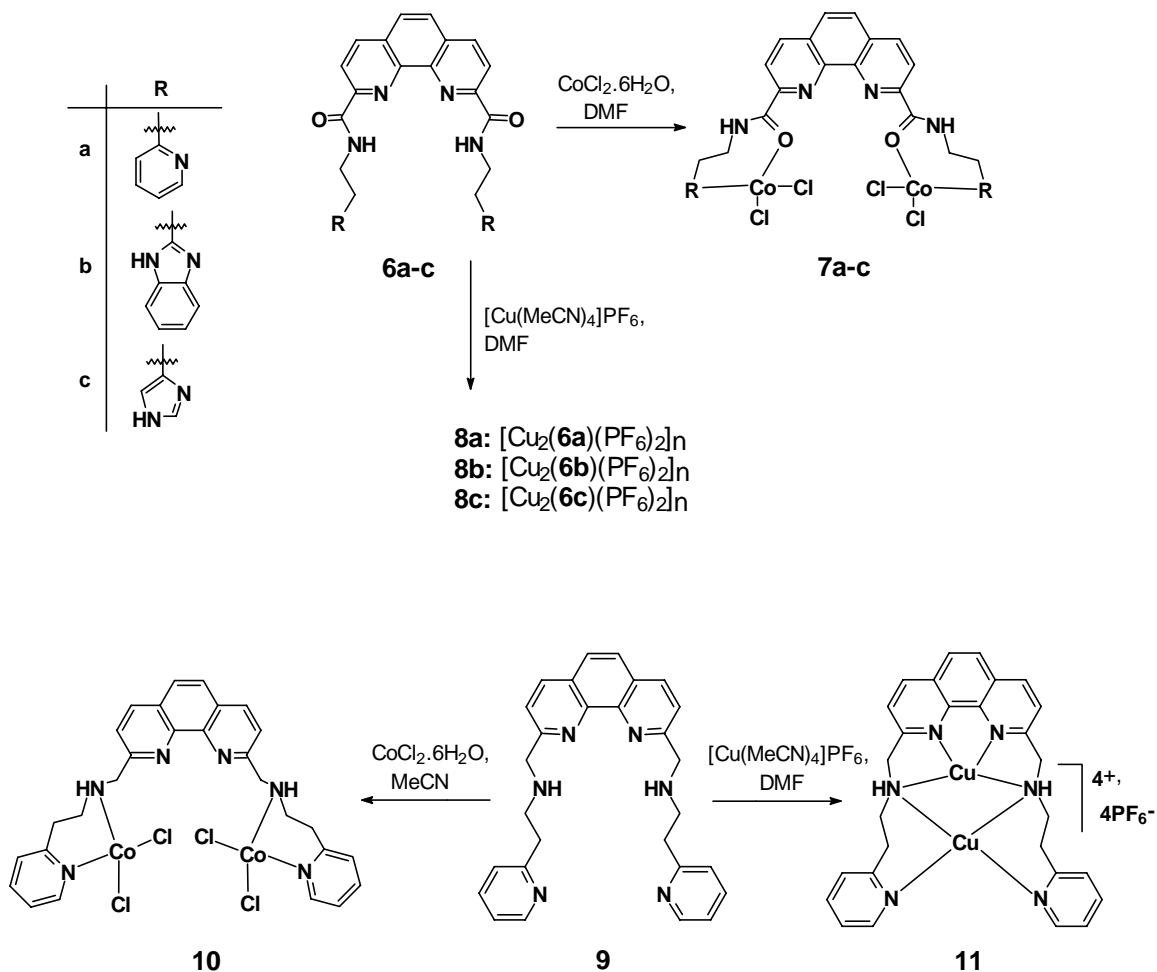
**Keywords:** Biomimetic, ligand, cobalt, copper, complexes, catalysis

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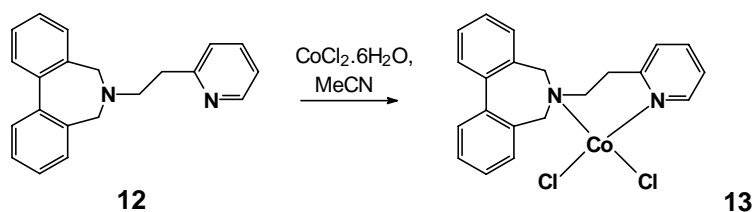
### Introduction

There is considerable interest in the development of biomimetic transition metal complexes.<sup>2-6</sup> Some time ago, Reglier *et al.*<sup>7</sup> described the synthesis and phenolase activity of a dinuclear Cu(I) complex, designed to model the enzyme tyrosinase, while very recently, Comba and co-workers<sup>8</sup> reported the X-ray crystal structures of three Cu(II) complexes which exhibit catecholase activity. Progress towards the elucidation of tyrosinase structures has been reviewed by van Gelder *et al.*,<sup>9</sup> and it is apparent that the active sites contain a pair of suitably spaced copper atoms capable of accommodating a bridged dioxygen molecule. In our own investigations in this area, we have explored the preparation of ligands which are capable of chelating two copper atoms and in which the co-ordinating moieties are separated by biphenyl,<sup>10</sup> 1,10-phenanthroline<sup>11</sup> and acyclic spacers.<sup>1</sup> Simple Co(II) complexes have also been shown to form metal complex-oxygen adducts,<sup>2</sup> and Co(II) complexes have been used to model biological processes.<sup>12</sup> In this communication, we report the preparation and catalytic activity of Co(II) and Cu(II) complexes of selected multidentate ligands.





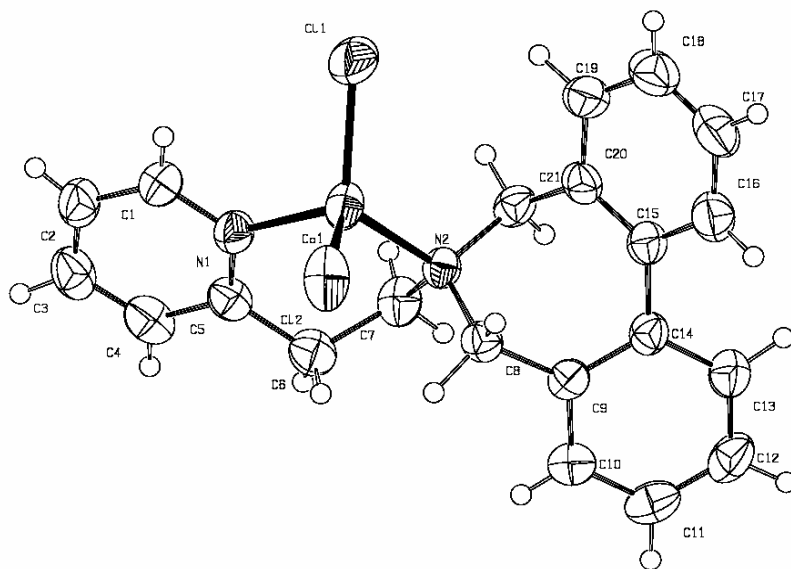
Scheme 2. 1,10-Phenanthroline-based ligands and complexes.



Scheme 3

The mid-IR frequency shifts (relative to the free ligands) of the amide NH and carbonyl (amide I) bands exhibited by the diamide complexes were used to establish whether coordination occurs through the amide nitrogen or oxygen atoms,<sup>13</sup> and whether coordination involving nitrogen donors is accompanied by deprotonation. Vibrational spectra were run in the far-IR region to determine the disposition (tetrahedral or octahedral) of the chloride ligands in the Co(II) complexes. Although the *two* Co–Cl bands characteristic of tetrahedral geometry about

the metal centre (at *ca.* 301 and 324  $\text{cm}^{-1}$ )<sup>14</sup> were not present in the IR spectra of the Co(II) complexes, a strong, broad band was observed, in each case, at *ca.* 300  $\text{cm}^{-1}$ . The presence of a single band is attributed to accidental degeneracy of the symmetric and antisymmetric Co–Cl stretches, and is considered to indicate a distorted tetrahedral cobalt geometry. This assumption is supported by the fact the amine complex **13** [shown by single crystal X-ray analysis to contain a tetrahedral cobalt ion (Figure 1)] exhibits a *single* far-IR band at 298  $\text{cm}^{-1}$ . The coordination geometry of cobalt complexes may also be inferred from characteristic absorption bands in the visible region, and absorption data for the complexes are summarised in Table 2. In all cases, the observed absorptions correspond to the  $^4A_2 \rightarrow ^4T_1(P)$  transition, which is characteristic of tetrahedral cobalt coordination; the fine structure evident in the spectra is attributed to spin-orbit coupling effects and to transitions involving doublet states.<sup>15</sup>



**Figure 1.** X-Ray crystal structure of complex **13**, showing the crystallographic numbering.

### Cyclic voltammetry

Cyclic voltammetry was used to confirm the oxidation level(s) of the metal centres in the dinuclear cobalt complexes **2**, **3**, **7a–c** and **10**. The observation (Table 3) of a single, strong peak at *ca.* 1 V (which is not exhibited by the corresponding ligand) indicates oxidation of Co(II) to Co(III) on the cyclic voltammetric time scale and suggests that, in each complex, the metal centres are symmetrically located. Comparison of the oxidation potentials of the biphenyl diamide complexes (**2** and **3**) with those of the 1,10-phenanthroline diamide complexes (**7a–c**) reveals that the latter have slightly higher oxidation potentials – an observation attributed to the

greater electron-withdrawing capacity of the 1,10-phenanthroline nucleus. The fact that the 1,10-phenanthroline diamine complex **10** exhibits a lower oxidation potential than the diamide complexes **7a–c** is attributed to electron-withdrawal by the carbonyl oxygen of the amide group, which renders the diamide complexes more resistant to oxidation. The complexity of the data has precluded unambiguous assignment of peaks in the cyclic voltammograms of the copper complexes.

### Catalytic activity

The ability of the complexes to oxidise phenol and/or catechol substrates using molecular oxygen was examined, using, as substrates, 2,4-di-*t*-butylphenol (DTBP) and 3,5-di-*t*-butylcatechol (DTBC). In addition to its oxidation to DTBC [which may be oxidised, in turn, to 3,5-di-*t*-butyl-*o*-quinone (DTBQ)], DTBP can also be oxidised to a coupled biphenyl product.<sup>16</sup> The catalytic activity of the various ligands was examined in DMF (chosen for its ability to dissolve the complexes), while <sup>1</sup>H NMR spectroscopy was used to detect the products of the oxidation reactions catalysed by the complexes. Given the excellent conversions observed for the Co(II) complexes (Table 1), the catalytic recyclability of these systems was also investigated.

**Table 1.** Catalytic data for the Co(II) and Cu(II) complexes

Compound	Catecholase activity <sup>a</sup>		
	Reaction time [h]	Conversion [%]	Recycled [%]
2	24	78(67) <sup>b</sup>	78
3	24	88(60) <sup>b</sup>	84
7a	24	67(26) <sup>b</sup>	67
7b	24	90(52) <sup>b</sup>	75
7c	24	92(47) <sup>b</sup>	96
10	24	89(30) <sup>b</sup>	53
4	120	13	- <sup>c</sup>
5	24	16 <sup>d</sup>	- <sup>c</sup>
8a	24	7	- <sup>c</sup>
8b	120	38 <sup>d</sup>	- <sup>c</sup>
8c	120	54 <sup>d</sup>	- <sup>c</sup>
11	120	0	- <sup>c</sup>

<sup>a</sup> Using DTBC as substrate in the presence of Et<sub>3</sub>N to afford the *o*-quinone. <sup>b</sup> After 3h. <sup>c</sup> Not determined. <sup>d</sup> In the absence of Et<sub>3</sub>N.

Of all the complexes examined, only the Cu(II) complexes **4**, **8a** and **8b** catalysed the oxidative coupling of DTBC to afford 3,3',5,5'-tetra-*t*-butyl-2,2'-dihydroxybiphenyl in low yield (9–13% conversion). A mechanism for such oxidative coupling of phenols has been proposed by Kushioka,<sup>16</sup> while the formation of other biphenyl products from the reactions of phenols with

copper complexes have been reported.<sup>17</sup> In contrast, all of the Co(II) complexes tested and all, but one, of the Cu(II) complexes catalysed conversion of DTBC to the corresponding *o*-quinone (Table 1). The Co(II) complexes proved to be significantly more efficient, generally effecting efficient conversion to the *o*-quinone within 24 h and with excellent recyclability.

Although all of the Cu(II) complexes, with the exception of complex 11, appear to be polymeric, the catalytic activity of complexes 4, 8a and 8b suggests that, in these cases at least, the copper ions are sufficiently close to permit dioxygen bridging and subsequent substrate binding; a Cu–Cu separation of *ca* 3.6 Å in the dioxygen bridged complexes is considered necessary for biomimetic activity.<sup>6</sup> Alternatively, polymer-monomer equilibria in solution could account for the presence of monomeric systems. In computer models of the Co(II) complexes 3 and 7b, the octahedral Co ions are separated by 3.1 Å and 3.4 Å, respectively. Interestingly, Yamami *et al.*<sup>12</sup> have reported Co–Co separations of 3.4–3.5 Å in the crystal structures of Co(II) complexes which catalyse the disproportionation of hydrogen peroxide.

**Table 2.** Electronic absorption bands for the cobalt complexes

Complex	Absorption [nm] (L mol <sup>-1</sup> cm <sup>-1</sup> )
2	596sh (478), 605 (535), 664 (775), 676 (775)
3	600sh (567), 613 (665), 657 (784), 678 (681)
7a	596sh (555), 604 (605), 665 (866), 677 (866)
7b	597sh (756), 611 (532), 656 (945), 676 (794)
7c	580sh (534), 608 (801), 629 (815), 677sh (548)
10	597sh (563), 604 (594), 666 (719), 678 (719)
13	576 (301), 621 (343), 638 (343)

**Table 3.** Measured peak potentials (V; oxidation side) for the biphenyl- and 1,10-phenanthroline-based cobalt complexes in DMF containing TEAP (Co<sup>II</sup>Co<sup>II</sup> → Co<sup>III</sup>Co<sup>III</sup>)

Complex	Scanning range [mV]	Scan rate [mV·s <sup>-1</sup> ]	Peak potentials from cyclic voltammograms vs Ag*Ag <sup>+</sup>
2	1600 to –1600	500	0.97
3	1250 to –1250	300	0.99
7a	1600 to –1600	400	1.08
7b	1250 to –1250	300	1.06
7c	1300 to –1300	400	1.02
10	1250 to –1250	300	0.86

## Experimental Section

**General Procedures.** Infrared spectra were recorded on a Perkin Elmer 2000 spectrophotometer

using potassium bromide discs (4000–400  $\text{cm}^{-1}$ ), hexachlorobutadiene mulls (HCBT; 4000–2000 and 1500–1250  $\text{cm}^{-1}$ ), polyethylene discs (500–30  $\text{cm}^{-1}$ ) or nujol mulls (500–30  $\text{cm}^{-1}$ ). NMR spectra were obtained from  $\text{CDCl}_3$  solutions on a Bruker AMX400 NMR spectrometer and are referenced using the solvent signals ( $\delta_{\text{H}}$  7.25 and  $\delta_{\text{C}}$  77.0 ppm). Electrochemical data were obtained using a Bio-Analytical Systems (BAS) CV-50 voltammograph. The measurements were carried out under nitrogen using freshly distilled, dried, degassed DMF. A glass carbon electrode (diameter = 3.0 mm) was used as the working electrode and a platinum wire as the counter electrode. A non-aqueous reference electrode was employed. The electrode solution for the non-aqueous reference electrode was prepared by dissolving 0.01 M  $\text{AgNO}_3$  in 0.1 M TEAP (tetraethylammonium perchlorate) in DMF, resulting in an  $\text{Ag}^+/\text{Ag}$  (TEAP/DMF) electrode; TEAP was employed as an electrolyte. Exploratory modelling of selected ligands and complexes was undertaken using the MSI Cerius2 platform on a Silicon Graphics O<sup>2</sup> computer.<sup>13</sup> The synthesis and characterisation of the ligands have been reported previously.<sup>10,11</sup>

**Cobalt complex 2.** To a stirred solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.22 g, 0.92 mmol) in MeOH (5 mL) was added dropwise a solution of 2,2'-bis[[2-(2-pyridyl)ethylamino]carbonyl]biphenyl **1a** (0.20 g, 0.44 mmol) in MeCN (5 mL), and the resulting mixture was stirred for 48 h.  $\text{Et}_2\text{O}$  was then added to precipitate **2** as a blue solid (0.21 g, 66%), mp 198–200 °C. IR:  $\nu_{\text{max}}$ (KBr) 1622  $\text{cm}^{-1}$  (CO);  $\nu_{\text{max}}$ (nujol) 306  $\text{cm}^{-1}$  (Co–Cl). Anal. Calcd. for  $\text{C}_{28}\text{H}_{26}\text{Cl}_4\text{Co}_2\text{N}_4\text{O}_2 \cdot \text{H}_2\text{O}$  (728.23): C, 46.2; H, 3.9; N, 7.7. Found: C, 46.3; H, 3.7; N, 7.5.

**Cobalt complex 3.** A clear, colourless solution of 2,2'-bis[[2-(2-benzimidazolyl)ethylamino]carbonyl]biphenyl **1b** (0.23 g, 0.44 mmol) in hot DMF (20 mL) was added to a stirred, blue solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.22 g, 0.92 mmol) in MeOH (5 mL). After stirring for 25 h, the volume of the reaction mixture was reduced to less than half the original volume by evaporating off the solvents under reduced pressure, and  $\text{Et}_2\text{O}$  was added to precipitate, as a blue solid **3** (0.24 g, 59%), mp >230 °C. IR:  $\nu_{\text{max}}$  (KBr) 3185 (amide NH), 1633  $\text{cm}^{-1}$  (CO);  $\nu_{\text{max}}$ (nujol) 295  $\text{cm}^{-1}$  (Co–Cl). Anal. Calcd. for  $\text{C}_{32}\text{H}_{28}\text{Cl}_4\text{Co}_2\text{N}_6\text{O}_2 \cdot 4\text{H}_2\text{O}$  (860.35): C, 44.7; H, 4.2; N, 9.8. Found: C, 44.6; H, 4.3; N, 10.2.

**Cobalt complex 7a.** A solution of 2,9-bis[[2-(2-pyridyl)ethylamino]carbonyl]-1,10-phenanthroline **6a** (0.20 g, 0.44 mmol) in a mixture of hot MeOH (10 mL) and MeCN (5 mL) was added dropwise to a purple solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.22 g, 0.92 mmol) in MeOH (4 mL). The colour of the reaction mixture changed to dark-green during stirring for ca. 23 h. The reaction mixture was concentrated *in vacuo* to half the original volume, and  $\text{Et}_2\text{O}$  was added to precipitate **7a** as a green solid (0.26 g, 100%), mp 78 °C. IR:  $\nu_{\text{max}}$  (KBr) 3274 (NH), 1645  $\text{cm}^{-1}$  (CO);  $\nu_{\text{max}}$  (nujol) 303  $\text{cm}^{-1}$  (Co–Cl). Anal. Calcd for  $\text{C}_{28}\text{H}_{24}\text{Cl}_4\text{Co}_2\text{N}_6\text{O}_2 \cdot \text{H}_2\text{O}$  (754.23): C, 44.6; H, 3.5; N, 11.1. Found: C, 44.8; H, 3.3; N, 11.1.

**Cobalt complex 7b.** A solution of 2,9-bis[[2-(2-benzimidazolyl)ethylamino]carbonyl]-1,10-phenanthroline **6b** (0.23 g, 0.40 mmol) in DMF (10 mL) was added dropwise to a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.20 g, 0.84 mmol) in DMF (5 mL). The resulting mixture was stirred for 52 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 precipitation of **7b** as a green powder (0.32 g, 57%), mp >230 °C. IR:  $\nu_{\max}$  (KBr) 3251 (amide NH), 1651 cm<sup>-1</sup> (CO);  $\nu_{\max}$  (nujol) 311 cm<sup>-1</sup> (Co–Cl). Anal. Calcd. for C<sub>32</sub>H<sub>26</sub>Cl<sub>4</sub>Co<sub>2</sub>N<sub>8</sub>O<sub>2</sub>·5H<sub>2</sub>O (904.37): C, 42.5; H, 4.0; N, 12.4. Found: C, 42.1; H, 3.6; N, 12.3.

**Cobalt complex 7c.** A solution of 2,9-bis[[2-(4-imidazolyl)ethylamino]carbonyl]-1,10-phenanthroline **6c** (0.19 g, 0.44 mmol) in hot DMF (15 mL) was added to a stirred solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.22 g, 0.92 mmol) in DMF (10 mL). The resulting dark-green mixture was stirred for 41 h, after which the volume of the reaction mixture was reduced to less than half by evaporating off the DMF under reduced pressure. Et<sub>2</sub>O was then added to precipitate **7c** as a dark-green solid (0.31 g, 94%), mp 206–210 °C IR:  $\nu_{\max}$ (KBr) 3259 (amide NH), 3121 (imidazole NH), 1645 cm<sup>-1</sup> (CO);  $\nu_{\max}$ (nujol) 299 cm<sup>-1</sup> (Co–Cl). Anal. Calcd. for: C<sub>24</sub>H<sub>22</sub>Cl<sub>4</sub>Co<sub>2</sub>N<sub>8</sub>O<sub>2</sub>·2H<sub>2</sub>O (750.20): C, 38.4; H, 3.5; N, 14.9. Found: C, 38.1; H, 3.6; N, 14.8.

**Cobalt complex 10.** A solution of 2,9-bis[[2-(2-pyridyl)ethylamino]methyl]-1,10-phenanthroline **9** (0.20 g, 0.44 mmol) in MeCN (10 mL) was added dropwise to a solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.22 g, 0.92 mmol) in MeCN (10 mL). The colour changed from bright blue to green and, after stirring for 18 h, **10** precipitated out as a green powder (0.19 g, 49%), mp >230 °C. IR:  $\nu_{\max}$  (KBr) 3398 cm<sup>-1</sup> (NH);  $\nu_{\max}$  (nujol) 311 cm<sup>-1</sup> (Co–Cl). Anal. Calcd. For C<sub>28</sub>H<sub>28</sub>Cl<sub>4</sub>Co<sub>2</sub>N<sub>6</sub>·5H<sub>2</sub>O (798.33): C, 42.1; H, 4.8; N, 10.5. Found: C, 41.8; H, 3.8; N, 10.1.

**Cobalt complex 13.** A solution of 1-[2-(2-pyridyl)ethyl]dibenzo[*c,e*]perhydroazepine **12** (0.19 g, 0.44 mmol) in MeCN (5 mL) was added dropwise to a solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.22 g, 0.92 mmol) in MeCN (10 mL), and the resulting mixture was stirred for 48 h. MeCN was allowed to evaporate off at room temperature, during which time, blue crystals of **13** precipitated and were filtered off (0.17 g, 89%), mp >250 °C. IR:  $\nu_{\max}$ (nujol) 298 cm<sup>-1</sup> (Co–Cl). Anal. Calcd. for C<sub>21</sub>H<sub>20</sub>Cl<sub>2</sub>CoN<sub>2</sub> (430.24): C, 58.6; H, 4.7; N, 6.5. Found: C, 57.8; H, 4.5; N, 6.6. The preparation of the copper(II) complexes is illustrated by the following examples.

**Copper complex 5.** A solution of 2,2'-bis[[2-(2-benzimidazolyl)ethylamino]carbonyl]biphenyl **1b** (0.23 g, 0.44 mmol) in hot, dry, degassed DMF (20 mL) was added dropwise to a stirred solution of [Cu(MeCN)<sub>4</sub>][PF<sub>6</sub>] (0.34 g, 0.92 mmol) in dry, degassed MeCN (10 mL). The resulting pale yellow-green solution gradually changed to a clear green colour as the reaction mixture was stirred under N<sub>2</sub> for 3.5 h. The addition of Et<sub>2</sub>O resulted in the precipitation of **5** as a light-green, polymeric solid (0.30 g, 66%), mp 198–202 °C. IR:  $\nu_{\max}$ (HCBBD) 3237 cm<sup>-1</sup> (amide NH);  $\nu_{\max}$ (nujol) 1651 (CO), 845 cm<sup>-1</sup> (PF<sub>6</sub>). Anal. Calcd. for [C<sub>32</sub>H<sub>28</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>·MeCN]<sub>n</sub> (986.69): C, 41.4; H, 3.2; N, 9.9. Found: C, 41.9; H, 3.9; N, 10.3.

**Copper complex 8a.** 2,9-Bis[[2-(2-pyridyl)ethylamino]carbonyl]-1,10-phenanthroline **6a** (0.20 g, 0.44 mmol) was dissolved in a mixture of hot, dry, degassed DMF (10 mL) and MeCN (15 mL). Dropwise addition of this solution to a colourless solution of [Cu(MeCN)<sub>4</sub>][PF<sub>6</sub>] (0.34 g, 0.92 mmol) in dry, degassed MeCN (10 mL) gave a dark-red mixture, the colour of which changed to dirty green upon stirring under N<sub>2</sub> for 6 h. The precipitated solid was filtered off and Et<sub>2</sub>O was added to the filtrate to precipitate the remainder of **8a**, which was filtered off as



a green powder (0.27 g, 62%), mp >230 °C. IR:  $\nu_{\max}$ (nujol) 1630 (CO), 842  $\text{cm}^{-1}$  ( $\text{PF}_6$ ). Anal. Calcd. for  $[\text{C}_{28}\text{H}_{24}\text{Cu}_2\text{N}_2(\text{PF}_6)_2]_n$  (893.56): C, 37.6; H, 2.7; N, 9.4. Found: C, 37.7; H, 2.0; N, 9.7. Physical and analytical data for the other copper(II) complexes are as follows.

**Copper complex 4.** Light-green solid (0.14 g, 20%), mp 212–214 °C. IR:  $\nu_{\max}$ (HCBBD) 3242 (amide NH), 3156  $\text{cm}^{-1}$  (imidazole NH);  $\nu_{\max}$ (nujol) 1652 (CO), 846  $\text{cm}^{-1}$  ( $\text{PF}_6$ ). Anal. Calcd. for  $[\text{C}_{24}\text{H}_{24}\text{Cu}_2\text{N}_6\text{O}_2(\text{PF}_6)_2 \cdot 5\text{H}_2\text{O}]_n$  (935.59): C, 30.8; H, 3.7; N, 9.0. Found: C, 30.8; H, 3.4; N, 8.8.

**Copper complex 8b.** Green-brown solid (0.29 g, 61%), mp >230 °C. IR:  $\nu_{\max}$ (HCBBD) 3227  $\text{cm}^{-1}$  (amide NH);  $\nu_{\max}$ (nujol) 1645 (CO), 846  $\text{cm}^{-1}$  ( $\text{PF}_6$ ). Anal. Calcd. for  $[\text{C}_{32}\text{H}_{26}\text{Cu}_2\text{N}_8\text{O}_2(\text{PF}_6)_2 \cdot 6\text{H}_2\text{O}]_n$  (1079.72): C, 35.6; H, 3.6; N, 10.4. Found: C, 35.4; H, 3.2; N, 10.3.

**Copper complex 8c.** Brown solid (0.15 g, 35%), mp >230 °C. IR:  $\nu_{\max}$ (HCBBD) 3157  $\text{cm}^{-1}$  (imidazole NH);  $\nu_{\max}$ (nujol) 1651 (CO), 845  $\text{cm}^{-1}$  ( $\text{PF}_6$ ). Anal. Calcd. for  $[\text{C}_{24}\text{H}_{22}\text{Cu}_2\text{N}_8\text{O}_2(\text{PF}_6)_2 \cdot 5\text{H}_2\text{O}]_n$  (961.59): C, 30.0; H, 3.4; N, 11.7. Found: C, 29.5; H, 3.0; N, 12.3.

**Copper complex 11.** Brown solid (0.38 g, 78%), mp >230 °C. IR:  $\nu_{\max}$ (HCBBD) 3273  $\text{cm}^{-1}$  (NH);  $\nu_{\max}$ (nujol) 842  $\text{cm}^{-1}$  ( $\text{PF}_6$ ). Anal. Calcd. for  $\text{C}_{28}\text{H}_{28}\text{Cu}_2\text{N}_6(\text{PF}_6)_4$  (1155.52): C, 29.1; H, 2.4; N, 7.3. Found: C, 30.2; H, 2.7; N, 7.4.

**X-Ray Crystal Data for 13.**  $\text{C}_{28}\text{H}_{30}\text{Cl}_2\text{CoN}_4$ ,  $M = 552.39$ ; monoclinic, space group  $\text{P}2(1)/n$ ;  $a = 8.7818$  (5),  $b = 16.09944$  (10),  $c = 13.7265$  (8) Å,  $\alpha = 90.00^\circ$ ;  $\beta = 91.86$  (10) $^\circ$ ;  $\gamma = 90.00^\circ$ ,  $V = 1939.7$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 1148$ ,  $D_c = 1.892$  g cm<sup>-3</sup>,  $\mu = 1.193$  mm<sup>-1</sup>. Data collection with graphite-monochromated Mo- $K_\alpha$  radiation,  $\lambda = 0.71073$  Å,  $T = 296$  (2) K,  $\theta$  range 1.95 to 28.30 $^\circ$ , 11620 reflections collected ( $-9 < h < 11$ ,  $-21 < k < 19$ ,  $-17 < l < 17$ ), 4349 unique with  $I > 2\sigma(I)$ . Hydrogen atoms were placed in calculated positions and the structure was solved by direct methods using SHELX-97;<sup>18</sup> full-matrix least-squares refinement converged at  $R_1 = 0.0581$ ,  $wR_2 = 0.1477$ , GOF = 1.074. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC150938. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**Catalytic studies.** The substrates DTBP and DTBC were added to solutions of the Co(II) complexes in DMF [or to suspensions of the polymeric Cu(II) complexes in dry DMF], typically containing Et<sub>3</sub>N (see Table 1), to give substrate:complex molar ratios of 100:1. The resulting mixtures were aerated by stirring vigorously for 1–5 d. 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 analysed as before.

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