# Synthesis and Crystal Structures of a Series of Amide Copper(II) Complexes*

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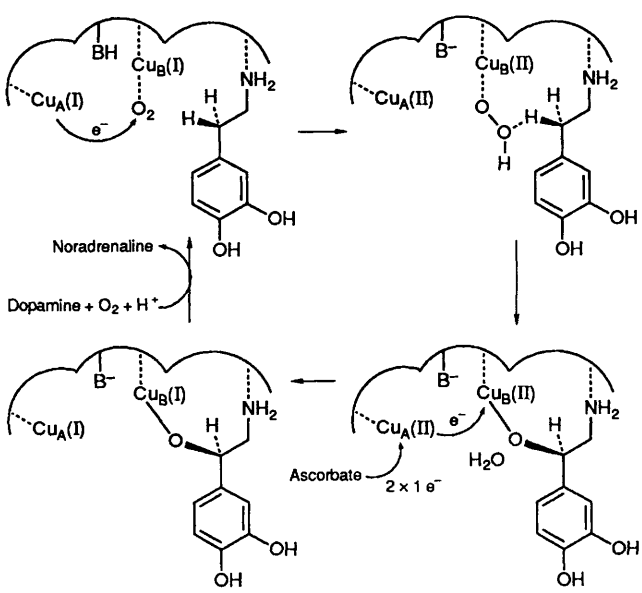
The synthesis and structural determination by X-ray crystallography of four amide copper(II) complexes has been performed: $[Cu\{OC[(CH_2)_2N(CH_2C_6H_4X)(CH_2CH_2C_5H_4N)]NH(CH_2)_nPh\}(solv)][CF_3SO_3]_2$ (X = H, solv = $H_2O$, $n$ = 2 **1** or 1 **2**; X = OH, solv = $H_2O$, $n$ = 2 **3**; solv = MeCN, $n$ = 1 **4**). In all complexes the co-ordination around the copper atom is a more or less distorted square-based pyramid where the three ligands of the square are unchanged: one oxygen atom of the amide group and two nitrogen atoms of the pyridine nucleus and of the tertiary amine. The fourth ligand is a water molecule (**1**–**3**) or an acetonitrile solvent molecule (**4**). The axial ligand is the oxygen atom of the phenolic group in complexes **3** and **4**, while in **1** and **2** this site is occupied by an oxygen atom of a triflate counter ion.

Current interest in copper complexes as model compounds for copper proteins[1] focuses on the design and synthesis of active-site mimics, in particular binuclear coupled copper-containing enzymes (type 3),[2] such as haemocyanin (dioxygen carrier)[3] and tyrosinase [monooxygenase, *ortho* hydroxylation of tyrosine into 3,4-dihydroxyphenylalanine (L-dopa)].[4] This approach will contribute to the elucidation of the factors that govern the structure[5] and the reactivity[6] of dioxygen at the dicopper centre.

Concerning dopamine β-hydroxylase,[7] a type 2 copper-ascorbate-dependent monooxygenase which catalyses the benzylic hydroxylation of dopamine into noradrenaline,† little information is available about the mode of binding of $O_2$ to the copper(I) sites. In contrast to the situation found in type 3 copper proteins, all available evidence coming from EPR,[8] ESEEM (electron spin echo envelope modulation spectroscopy),[9] EXAFS (extended X-ray absorption fine structure)[10] and biochemistry studies[11] suggests that dopamine β-hydroxylase contains two inequivalent copper atoms per active site with a $Cu_A(His)_3(H_2O)\cdots Cu_B(His)_2X(H_2O)$ type configuration in the oxidized copper(II) enzyme. According to these studies, the identity of X is consistent with either a N- (His) or an O-donor ligand. The $Cu_A$ site is proposed to be at the core of a reductant site where ascorbate binds and delivers one electron at a time. The $Cu_B$ centre, at a distance greater than 4 Å, is involved in dioxygen fixation and is responsible, *via* a copper(II) hydroperoxo species,[12] for the hydroxylation of dopamine (Scheme 1).

In the course of our studies on the metallic centre of copper-containing monooxygenase[13] β-hydroxylase we have undertaken the chemical modelling of the $Cu_B$(II) site of dopamine. We report here the first step of this work concerning the synthesis and the structural determination by X-ray crystallography of four copper(II) complexes featuring two nitrogen-donor ligands and one or two oxygen-donor ligands (phenol and/or amide groups).




**Scheme 1** Postulated dopamine β-hydroxylase mechanism involving two distinct copper sites with separate functions

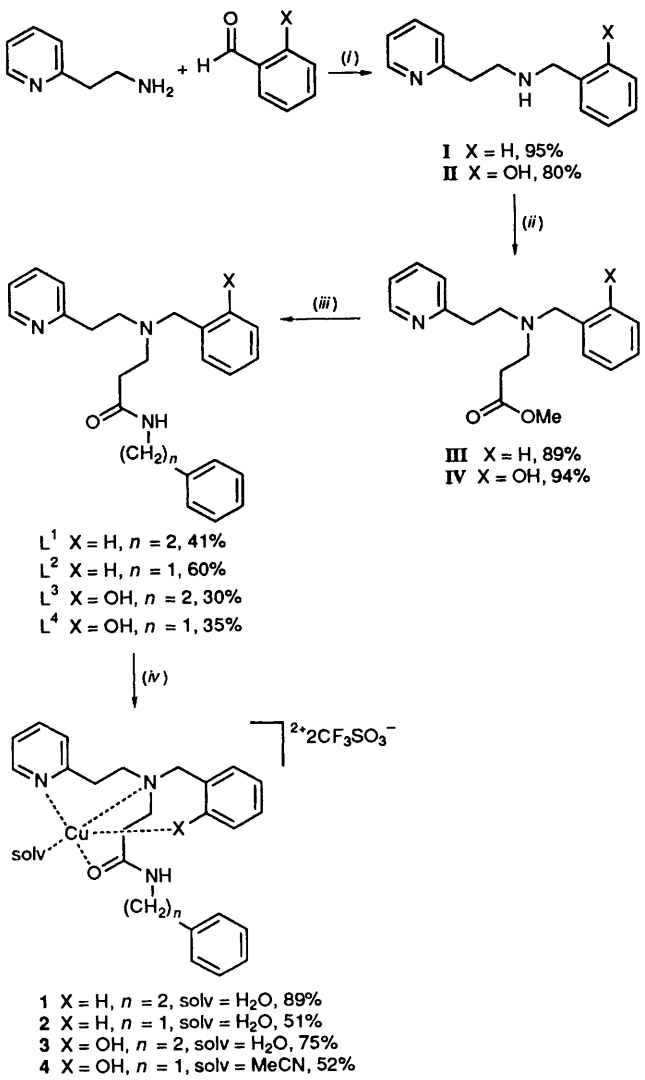
## Results and Discussion

*Synthesis.*—Ligands $L^1$–$L^4$ were synthesised in three steps as shown in Scheme 2. Reduction by $NaBH_4$ in ethanol medium of the imine intermediate formed by interaction of 2-(2-pyridyl)-ethylamine and the corresponding aromatic aldehyde yields secondary amines **I** and **II** which are used without purification for the following step. Their Michael addition to methyl acrylate affords in good yields (89–94%) β-aminoesters **III** and **IV**. Amidations in a NaOMe–MeOH medium of those esters by 2-phenylethylamine or benzylamine yield ligands $L^1$–$L^4$. The relatively poor yield (30–60%) of this step is due to a secondary reaction promoted by NaOMe which transform the amino-esters into secondary amines **I** and **II** by a retro Michael process.

Interaction of ligands $L^1$–$L^4$ with copper(II) trifluoromethanesulfonate (triflate) in anhydrous tetrahydrofuran affords copper(II) complexes **1**–**4** which are isolated as blue solids after tetrahydrofuran evaporation. Recrystallizations at 4 °C of saturated acetonitrile solutions of the complexes using diethyl ether vapour diffusion give rise to suitable crystals for X-ray analysis.

* *Supplementary data available:* See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

† Dopamine = 4-(2-aminoethyl)benzene-1,2-diol; noradrenaline = 4-(2-amino-1-hydroxyethyl)benzene-1,2-diol.




**Scheme 2** Synthesis of copper(II) complexes **1**–**4**. (*i*) $NaBH_4$, EtOH; (*ii*) methylacrylate; (*iii*) amine, MeOH–NaOMe; (*iv*) $Cu(CF_3SO_3)_2$, thf

*Structural Description of Complexes* **1**–**4**.—The structures are composed of discrete copper cations and triflate counter ions. However one triflate ion is linked, *via* a Cu–O bond, to the cation in crystals. The complexes **1**–**3** adopt an identical geometry as can be seen in Figs. 1–3 On the contrary, the conformation of complex **4** is different owing to an inversion of the relative position of the phenyl and pyridine ligands (Fig. 4).

Experimental details of the structure determinations are given in Table 1, atomic coordinates in Table 2 and distances and angles around the copper atoms in complexes **1**–**4** in Table 3. The distances and angles are very similar to those found in a series of copper(II) mono-[14] and bi-nuclear five-co-ordinated complexes with a longer apical bond.[15] The co-ordination geometry is best described by a square-based pyramid which is more or less distorted. For all these complexes three ligands of the square plane are unchanged: one oxygen of the amide group, and two nitrogen atoms of the pyridine nucleus and the tertiary amine. The fourth ligand is a water molecule for complexes **1**–**3**, or an acetonitrile solvent molecule for **4**. The axial ligand is the oxygen atom of the phenolic group for **3** and **4** while in the complexes **1** and **2** this site is occupied by one oxygen atom of the triflate anion. For complexes **1**, **3** and **4** the central copper atom is out of the plane, towards the fifth ligand. However when the fifth ligand is the phenolic group as in complexes **3** and **4**, the distance of the copper to the mean square plane remains short: 0.045(1) and 0.016(4) Å respectively, compared to 0.089(1) Å for **1** with triflate as fifth ligand. In the case of complex **2** the copper atom is in the plane formed by two nitrogen atoms and the oxygen atom of the amide group, the water molecule being 0.43(1) Å from this plane.

Amide groups are well known to offer two potential binding sites for metal-ion complexation (O- *vs.* N-metallation).[16] For neutral amides complexation occurs generally at the oxygen atom which is the most basic site. Amide deprotonation makes the nitrogen more basic than the oxygen atom and complexation at nitrogen can be observed. In agreement with these results, the crystal structure determination of complexes **1**–**4**, where the amide groups are protonated, reveals that the copper centre is always bonded to the oxygen atom.

The triflate plays different roles in the four complexes. In **4** it is only a counter ion. In **1** it is involved in the co-ordination of the copper atom, the oxygen O(1) being the fifth axial ligand. Moreover O(2) is linked to the water molecule O(8) by a

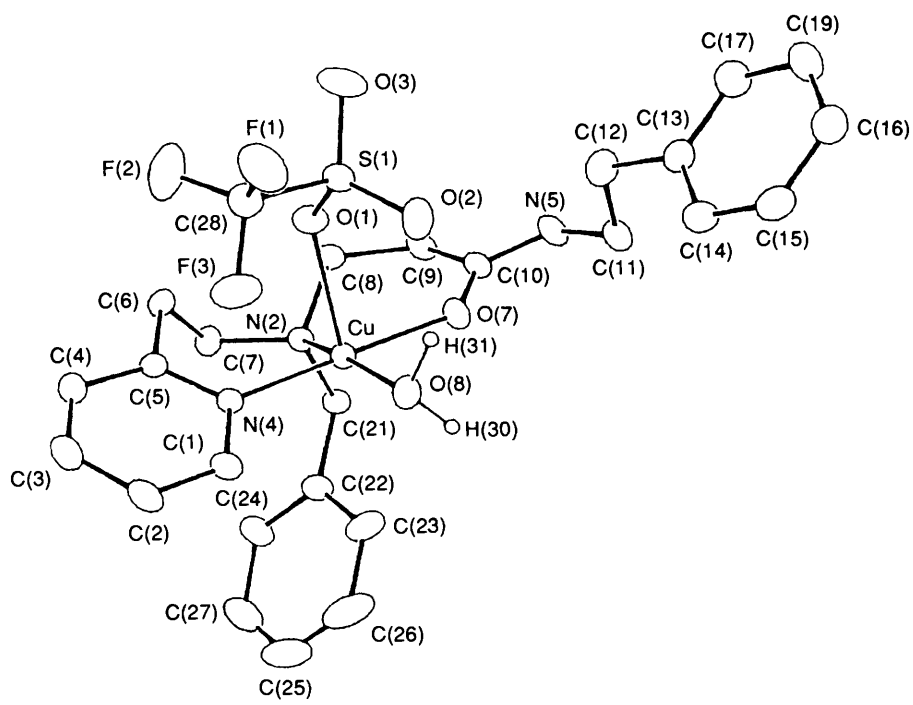



**Fig. 1** An ORTEP perspective view of complex **1** (the second triflate counter ion has been omitted for clarity)

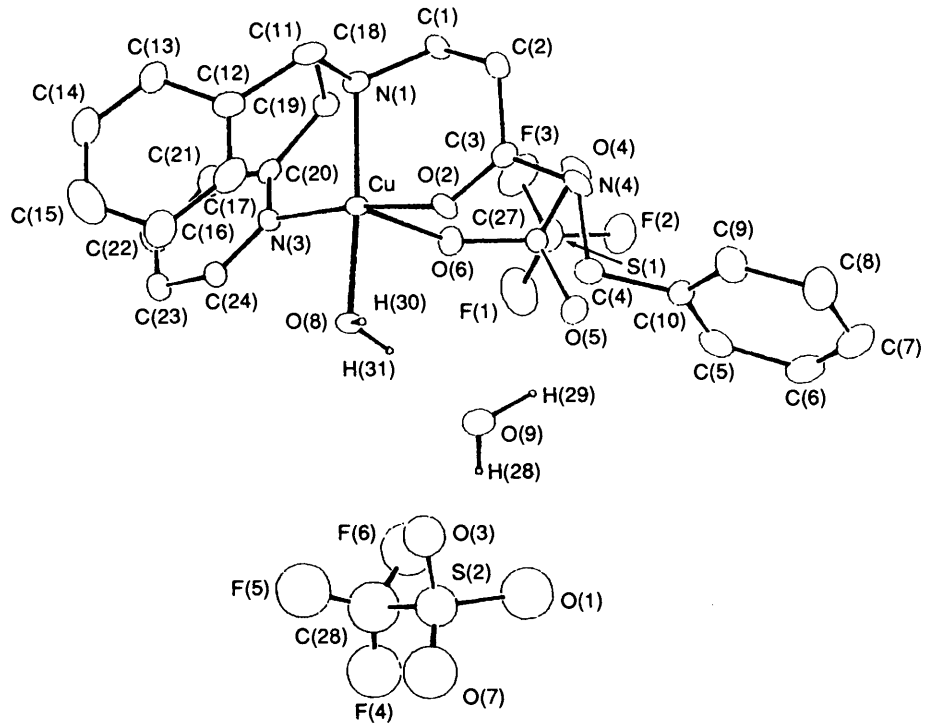






**Fig. 2** An ORTEP perspective view of complex **2**

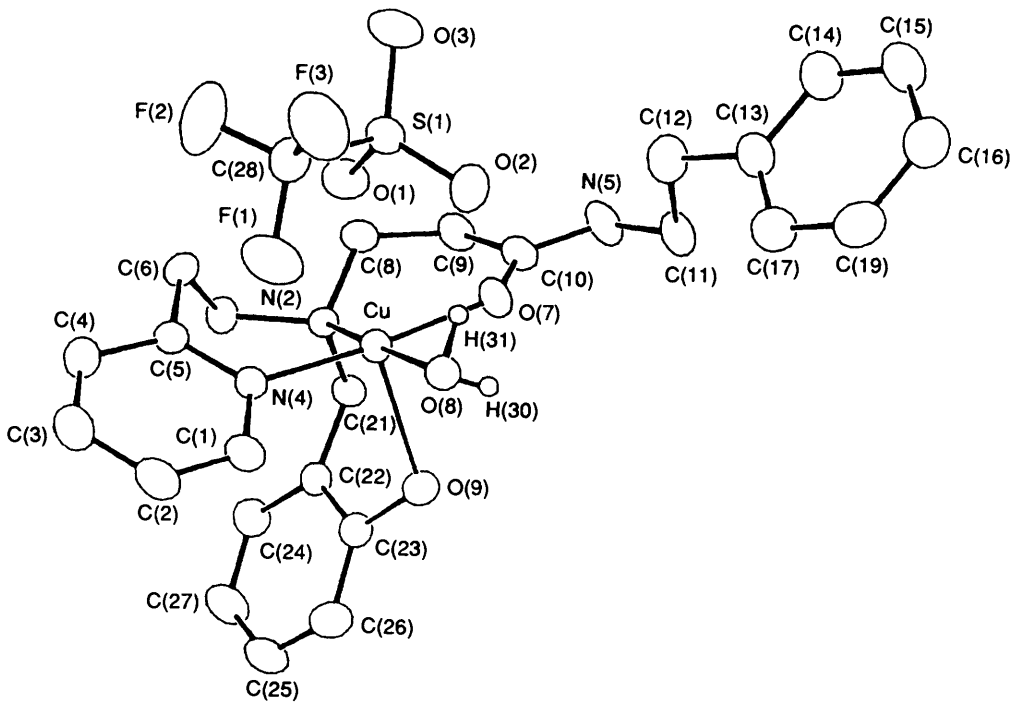



**Fig. 3** An ORTEP perspective view of complex **3** (the second triflate counter ion has been omitted for clarity)

hydrogen bond [O(2)···H(31)–O(8) 2.83(1) Å, O–H–O 155.0(6)°]. This hydrogen bond is also found in complex **3** [O(2)···H(31)–O(8) 2.77(1) Å, O–H–O 169.8(8)°] but not in **2**. In the latter case the water molecule linked to the copper atom is hydrogen bonded with O(9) of the second water molecule [O(8)···O(9) 2.75(2) Å. O(8)–H(30)···O(9) and O(8)–H(31)···O(9) 156.8(8) and 157.1(7)° respectively]. This water molecule is also hydrogen bonded with atoms O(5) and O(3) of the triflate ions [O(9)–H(29)···O(3) 2.72(2) Å, O–H–O 146(1)°; O(9)–H(28)···O(5) 2.82(2) Å, O–H–O 147.7(8)°].

It is worthwhile to note that these compounds, which have been prepared and crystallized under very similar conditions, exhibit molecular conformations with striking similarities and/or differences. Thus, complexes **3** and **4** which differ by only one $CH_2$ (benzylamine instead of a phenylethylamine) have a different molecular and crystal structure. On the other hand **1** and **3**, which crystallize as isomorphous crystals, show the same relative orientation of the ligands. The substitution of a phenolic group by a phenyl is balanced by a swing of the triflate ion around the O(2)···H(31)–O(8) hydrogen bond, allowing the oxygen O(1) to be engaged in the co-ordination sphere as an

**Table 1** Experimental details of the crystal structure determinations

| Complex | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Formula | $C_{27}H_{31}CuF_6N_3O_8S_2$ | $C_{26}H_{31}CuF_6N_3O_9S_2$ | $C_{27}H_{31}CuF_6N_3O_9S_2$ | $C_{28}H_{30}CuF_6N_4O_8S_2$ |
| $M$ | 767.22 | 771.21 | 783.22 | 792.23 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ |
| $a$/Å | 11.716(6) | 12.251(6) | 11.583(4) | 12.899(5) |
| $b$/Å | 17.400(8) | 12.307(6) | 17.368(6) | 14.027(8) |
| $c$/Å | 16.234(8) | 11.795(6) | 16.420(6) | 11.694(3) |
| $\alpha$/° | 90 | 107.29(5) | 90 | 108.88(4) |
| $\beta$/° | 99.97(5) | 93.11(5) | 99.06(4) | 102.99(4) |
| $\gamma$/° | 90 | 102.54(5) | 90 | 100.55(4) |
| $U$/Å$^3$ | 3259(4) | 1644(2) | 3262(3) | 1874(3) |
| $Z$ | 4 | 2 | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.52 | 1.56 | 1.59 | 1.40 |
| $F$(000) | 1576 | 767.18 | 1628 | 752 |
| Colour | Blue | Blue | Blue | Blue |
| Crystal size/mm | 0.4 × 0.4 × 0.5 | 0.4 × 0.3 × 0.5 | 0.3 × 0.4 × 0.5 | 0.5 × 0.4 × 0.3 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$ | 8.730 | 8.621 | 8.825 | 7.597 |
| Total no. of unique data | 4817 | 4834 | 4331 | 2732 |
| No. with $F^2 > 3\sigma(F^2)$ | 3376 | 3030 | 2827 | 1602 |
| $R^a$ | 0.044 | 0.113 | 0.041 | 0.113 |
| $R'^b$ | 0.054 | 0.156 | 0.049 | 0.140 |
| Goodness of fit$^c$ | 1.889 | 4.968 | 1.577 | 5.849 |
| Largest shift/e.s.d in final cycle | 0.54 | 0.73 | 0.37 | 0.04 |
| Largest peak/e Å$^{-3}$ | 0.35 | 0.42 | 0.35 | 0.50 |

$^a$ $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b$ $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/\sigma^2(|F_c|)$. $^c$ Goodness of fit $= w(|F_o| - |F_c|)^2/(\Sigma w|F_o|^2)^{\frac{1}{2}}$.

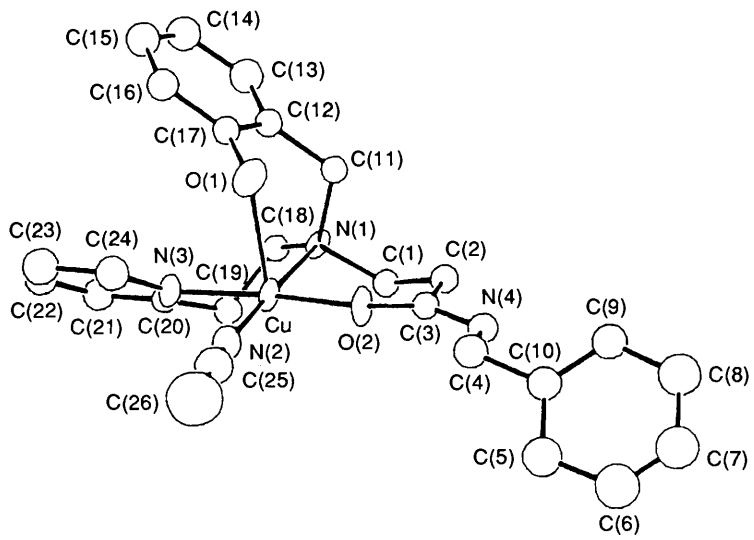
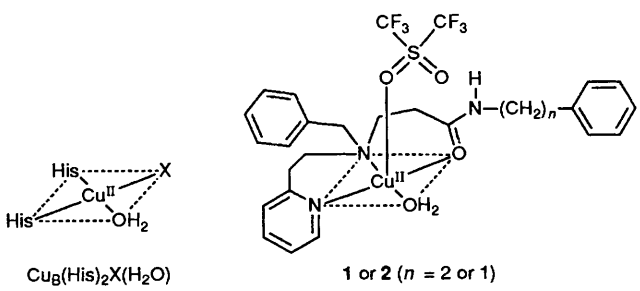



**Fig. 4** An ORTEP perspective view of complex **4** (the triflate counter ions have been omitted for clarity)




**Scheme 3**

axial ligand. In both structures the free phenyl and the blocked phenolic group exhibit the same orientation with respect to the rest of the structure.

## Conclusion

As mentioned above, structural studies have suggested that $Cu_B(II)$ is co-ordinated to two N-donor ligands (His), a water molecule and an additional N- or O-donor ligand completing the four-co-ordination. Except for the long ($\approx$2.4 Å) interaction of the $Cu^{II}$ with the triflate counter ions, we have found the same environment in complexes **1** and **2** showing these could be good structural models for $Cu_B(II)$ EXAFS studies (Scheme 3). On the other hand, for complex **1**, the presence of a phenylethylamide group fixed on the ligand will permit, after reaction with hydrogen peroxide, study of the oxygen transfer of the $Cu^{II}OOH$ centre to the phenylethylamide group.

## Experimental

(*a*) *General Materials and Procedures.*—All materials were commercial products and used without further purification unless otherwise noted. All solvents were freshly distilled under

nitrogen: methanol and ethanol from magnesium, tetrahydrofuran and diethyl ether from sodium–benzophenone, dichloromethane from $P_2O_5$ and acetonitrile from $CaH_2$. Elemental analyses were obtained on a CHN Technicon microanalyser. Infrared spectra were recorded on Nicolet MX 5 and Philips PU 9706 spectrometers, UV/VIS spectra on a Philips PU 8720 spectrometer, and NMR spectra on a Bruker AC-200 for $^1H$ and Varian XL-200 spectrometer for $^{13}C$.

(*b*) *Preparations.*—N-*Benzyl*-2-(2-*pyridyl*)*ethylamine* **I**. Benzaldehyde (12.4 g, 117 mmol) and 2-(2-aminoethyl)pyridine (10 g, 82 mmol) were refluxed in absolute ethanol (75 $cm^3$) for 30 min. After cooling to room temperature, a suspension of $NaBH_4$ (8.18 g, 216 mmol) in 98% ethanol (75 $cm^3$) was added dropwise at moderate rate. This mixture was allowed to stand at room temperature for 2 h. After this period, 1 mol $dm^{-3}$ HCl solution was added to pH 7. The heterogeneous mixture was filtered, the ethanol evaporated under vacuum and 1 mol $dm^{-3}$ HCl (200 $cm^3$) added. The aqueous acidic layer was washed with dichloromethane (2 × 200 $cm^3$), made basic by addition of 3 mol $dm^{-3}$ NaOH (150 $cm^3$) and extracted with dichloromethane (3 × 150 $cm^3$). The combined organic layers were dried over sodium sulfate. Dichloromethane evaporation under vacuum afforded crude amine **I** (16.5 g, 95%); $\nu_{max}$(neat) 3500 (NH), 1600 (C=N), 1570, 1480 and 1440 $cm^{-1}$ (C=C); NMR ($CDCl_3$, standard $SiMe_4$): $^1H$(200 MHz), δ 8.53 (1 H, d, *J* 4.1, 1 CH of $C_5H_4N$), 7.55 (1 H, td, *J* 7.6, 1.7 Hz, 1 CH of $C_5H_4N$), 7.29 (5 H, m, $C_6H_5$), 7.11 (2 H, m, 2 CH of $C_5H_4N$), 3.83 (2 H, s, $C_6H_5CH_2N$), 3.03 (4 H, m, $C_5H_4NCH_2CH_2N$) and 1.91 (1 H, br s, NH); $^{13}C$(50 MHz), δ 160.12 (C), 149.15 (CH), 140.19 (C), 136.15 (CH), 128.19 (2 CH), 127.94 (2 CH), 126.19 (CH), 123.11 (CH), 121.06 (CH), 53.70 ($CH_2$), 48.69 ($CH_2$) and 38.29 ($CH_2$).

N-2-*Hydroxybenzyl*-2-(2-*pyridyl*)*ethylamine* **II**. By a procedure analogous to the preparation of **I**, salicylaldehyde (14.2 g, 117 mmol), 2-(2-aminoethyl)pyridine (10 g, 82 mmol) and $NaBH_4$ (8.18 g, 216 mmol) afforded the secondary amine **II** (15 g, 80%); $\nu_{max}$(neat) 3300 (OH), 1600 (C=N), 1520, 1480 and 1440 $cm^{-1}$ (C=C); NMR ($CDCl_3$, standard $SiMe_4$): $^1H$(200 MHz), δ 8.53 (1 H, dd, *J* 4.7, 1.6, 1 CH of $C_5H_4N$), 7.61 (1 H, td, *J* 7.7, 1.8, 1 CH of $C_5H_4N$), 7.17–7.11 (5 H, m, 2 CH of $C_5H_4N$, CH of $C_6H_4OH$ and OH), 6.98 (1 H, d, *J* 6.1, 1 CH of $C_6H_4OH$), 6.78 (1 H, t, *J* 7.2, CH of $C_6H_4OH$), 6.80 (1 H, m, NH), 6.75 (1 H, t, *J* 7.2 Hz, CH of $C_6H_4OH$), 4.00 (2 H, s, *o*-$HOC_6H_4CH_2N$) and 3.06 (4 H, m, $C_5H_4NCH_2CH_2N$]; $^{13}C$(50 MHz), δ 159.51 (C), 158.28 (C), 149.29 (CH), 136.54 (CH), 128.56 (CH), 128.29 (CH), 123.38 (CH), 122.51 (C), 121.50 (CH), 118.54 (CH), 116.30 (CH), 52.44 ($CH_2$), 47.64 ($CH_2$) and 37.17 ($CH_2$).

*Methyl* 3-[N-*benzyl*-N-2-(2-*pyridyl*)*ethylamino*]*propanoate* **III**. The secondary amine **I** (10 g, 47 mmol) was refluxed for 8 h in freshly distilled methyl acrylate (10 $cm^3$). After evaporation under vacuum of the excess of methyl acrylate, flash chromatography [silica gel, $CH_2Cl_2$–MeOH (95:5)] yielded ester **III** (12.5 g, 89%); $\nu_{max}$(neat) 1740 (C=O), 1540, 1490 and 1460 $cm^{-1}$ (C=C); NMR ($CDCl_3$, standard $SiMe_4$): $^1H$(200 MHz), δ 8.51 (1 H, d, *J* 5, CH of $C_5H_4N$), 7.70 (1 H, td, *J* 7.5, 1.8, CH of $C_5H_4N$), 7.32 (5 H, m, $C_6H_5$), 4.31 (2 H, s, $C_6H_5CH_2N$), 3.70 (3 H, s, $CO_2CH_3$), 3.06 (4 H, m, $C_5H_4NCH_2CH_2N$), 3.21 (2 H, t, *J* 7.3, $NCH_2CH_2CO_2Me$) and 3.05 (2 H, t, *J* 7.3 Hz, $NCH_2CH_2CO_2Me$); $^{13}C$(50 MHz), δ 172.63 (C=O), 160.17 (C), 148.79 (CH), 139.30 (C), 136.73 (C), 128.33 (2 CH), 127.81 (2 CH), 126.53 (CH), 123.03 (CH), 120.68 (CH), 58.09 ($CH_2$), 53.31 ($CH_2$), 51.05 ($CH_2$), 48.96 ($CH_3$), 35.62 ($CH_2$) and 32.27 ($CH_2$).

*Methyl* 3-[N-2-*hydroxybenzyl*-N-2-(2-*pyridyl*)*ethylamino*]-*propanoate* **IV**. By a procedure analogous to the synthesis of **III**, the secondary amine **II** (10 g, 44 mmol) was transformed into **IV** (13 g, 94%); NMR ($CDCl_3$, standard $SiMe_4$): $^1H$(200 MHz), δ 8.50 (1 H, d, *J* 3.6, CH of $C_5H_4N$), 7.58 (1 H, t, *J* 7.6, CH of $C_5H_4N$), 7.14 (3 H, m, 3 CH of $C_6H_5$), 6.96 (1 H, d, *J* 6.9, CH of $C_6H_4OH$), 6.74 (2 H, m, CH of $C_6H_4OH$), 3.81 (2 H, s, *o*-$HOC_6H_4CH_2$), 3.62 (3 H, s, $CO_2CH_3$), 3.00 (4 H, s, $C_5H_4NCH_2CH_2N$), 2.91 (2 H, t, *J* 7.3, $NCH_2CH_2CO_2Me$) and 2.52 (2 H, t, *J* 7.1 Hz, $NCH_2CH_2CO_2Me$); $^{13}C$(50 MHz), δ 172.16 (C=O), 159.14 (C), 157.57 (C), 149.24 (CH), 136.45 (CH), 128.77 (CH), 128.61 (CH), 123.30 (CH), 121.61 (CH), 121.40 (CH), 119.12 (CH), 116.10 (CH), 57.81 ($CH_2$), 53.00 ($CH_2$), 51.64 ($CH_3$), 48.73 ($CH_2$), 34.77 ($CH_2$) and 31.30 ($CH_2$).

3-[N-*Benzyl*-N-2-(2-*pyridyl*)*ethylamino*]-N′-(2-*phenylethyl*)-*propanamide* $L^1$. To anhydrous methanol (20 $cm^3$) was added metallic sodium (0.8 g, 35 mmol). When all sodium had been transformed into NaOMe, 2-phenylethylamine (4.4 g, 36 mmol) was added. After stirring for 1 h at room temperature, **III** (11 g, 37 mmol) was added. The mixture was allowed to stand at room temperature for 48 h. After methanol evaporation under reduced pressure, the residue was dissolved in dichloromethane, washed with brine and dried over magnesium sulfate. After solvent evaporation, flash chromatography [silica gel, $CH_2Cl_2$–MeOH (95:5)] afforded amide $L^1$ (5.78 g, 41%); $\nu_{max}$(neat) 3300 (NH) and 1660 $cm^{-1}$ (C=O); NMR ($CDCl_3$, standard $SiMe_4$): $^1H$(200 MHz), δ 8.50 (1 H, dd, *J* 4.9, 0.9, CH of $C_5H_4N$), 7.63 (1 H, br s, CONH), 7.57 (1 H, td, *J* 7.5, 1.8, CH of $C_5H_4N$), 7.37–7.02 (12 H, m, 2 $C_6H_5$ and 2 CH of $C_5H_4N$), 3.58 (2 H, s, $C_6H_5CH_2N$), 3.30 (2 H, q, *J* 6.7, $C_6H_5CH_2CH_2NHCO$), 2.89 (4 H, s, $C_5H_4NCH_2CH_2N$), 2.72 (2 H, t, *J* 5.6, $NCH_2CH_2CONH$), 2.66 (2 H, t, *J* 7.3, $C_6H_5CH_2CH_2NHCO$) and 2.36 (2 H, t, *J* 5.6 Hz, $NCH_2CH_2CONH$); $^{13}C$(50 MHz), δ 172.37 (C=O), 160.00 (C), 149.31 (CH), 139.33 (C), 137.86 (CH), 136.36 (CH), 129.25 (2 CH), 128.74 (2 CH), 128.48 (2 CH), 128.43 (2 CH), 127.39 (CH), 126.34 (CH), 123.19 (CH), 121.31 (CH), 58.31 ($CH_2$), 52.78 ($CH_2$), 49.70 ($CH_2$), 40.26 ($CH_2$), 35.70 ($CH_2$), 34.88 ($CH_2$) and 33.01 ($CH_2$).

3-[N-*Benzyl*-N-2-(2-*pyridyl*)*ethylamino*]-N′-*benzylpropanamide* $L^2$. By a procedure analogous to the synthesis of amide $L^2$, ester **IV** (11 g, 37 mmol) and benzylamine (3.9 g, 36 mmol) were transformed into amide $L^2$ (8.12 g, 60%); $\nu_{max}$(neat) 3240 (NH), 1660 (C=O), 1550 (C=N), 1480 and 1430 $cm^{-1}$ (C=C); NMR ($CDCl_3$, standard $SiMe_4$): $^1H$(200 MHz), δ 8.44 (1 H, d, *J* 5, 1 CH of $C_5H_4N$), 8.22 (1 H, br s, 1 CONH), 7.51 (1 H, td, *J* 7.0, 2.0, 1 CH of $C_5H_4N$), 7.28 (5 H, m, $C_6H_5$), 7.20 (5 H, m, $C_6H_5$), 7.04 (2 H, m, 2 CH of $C_5H_4N$), 4.27 (2 H, d, *J* 2, $C_6H_5CH_2NHCO$), 3.60 (2 H, s, $C_6H_5CH_2N$), 2.89 (4 H, s, $C_5H_4NCH_2CH_2N$), 2.80 (2 H, t, *J* 6, $NCH_2CH_2CONH$) and 2.43 (2 H, t, *J* 6 Hz, $NCH_2CH_2CONH$); $^{13}C$(50 MHz), δ 172.24 (C=O), 159.92 (C), 149.30 (CH), 138.71 (C), 137.90 (CH), 136.00 (CH), 129.07 (2 CH), 128.55 (2 CH), 128.40 (2 CH), 127.82 (CH), 127.28 (2 CH), 127.20 (CH), 123.12 (CH), 121.27 (CH), 58.52 ($CH_2$), 52.91 ($CH_2$), 50.00 ($CH_2$), 43.10 ($CH_2$), 35.11 ($CH_2$) and 33.04 ($CH_2$).

3-[N-2-*Hydroxybenzyl*-N-2-(2-*pyridyl*)*ethylamino*]-N′-(2-*phenylethyl*)*propanamide* $L^3$. By a procedure analogous to the synthesis of amide $L^1$, ester **IV** (12 g, 38 mmol) and 2-phenylethylamine (4.4 g, 36 mmol) were transformed into amide $L^3$ (4.4 g, 30%); $\nu_{max}$(neat) 3410 (OH), 1655 (C=O), 1590 (C=N), 1509, 1470 and 1450 $cm^{-1}$ (C=C); NMR ($CDCl_3$, standard $SiMe_4$): $^1H$(200 MHz), δ 8.47 (1 H, d, *J* 4.2, CH of $C_5H_4N$), 7.58 (1 H, td, *J* 7.8, 1.8, CH of $C_5H_4N$), 7.42–7.08 (9 H, m, $C_6H_5$, 2 CH of $C_5H_4N$, CH of $C_6H_4OH$ and OH), 6.96 (1 H, dd, *J* 7.9, 1.7, CH of $C_6H_4OH$), 6.79 (d, *J* 8 Hz, CH of $C_6H_4OH$), 6.77 (1 H, t, *J* 7.2, CH of $C_6H_4OH$), 5.95 (1 H, br s, CONH), 3.80 (2 H, s, *o*-$HOC_6H_4CH_2$), 3.40 (2 H, q, *J* 6.9, $C_6H_5CH_2CH_2NHCO$), 3.00 (4 H, m, $C_5H_4NCH_2CH_2N$), 2.90 (2 H, t, *J* 7.1, $NCH_2CH_2CONH$), 2.75 (2 H, t, *J* 6.9, $C_6H_5CH_2CH_2NHCO$) and 2.30 (2 H, t, *J* 7.1 Hz, $NCH_2CH_2CONH$); $^{13}C$(50 MHz), δ 171.18 (C=O), 159.38 (C), 157.51 (C), 149.06 (CH), 138.98 (C), 136.59 (CH), 129.00 (2 CH), 128.82 (CH), 128.67 (CH), 128.47 (CH), 126.32 (2 CH), 123.44 (CH), 122.05 (C), 121.45 (CH), 119.21 (CH), 116.19 (CH), 57.67 ($CH_2$), 53.25 ($CH_2$), 49.74 ($CH_2$), 40.64 ($CH_2$), 35.51 ($CH_2$), 34.72 ($CH_2$) and 33.68 ($CH_2$).

3-[N-2-*Hydroxybenzyl*-N-2-(2-*pyridyl*)*ethylamino*]-N′-*benzylpropanamide* $L^4$. By a procedure analogous to the synthesis of amide $L^1$, ester **IV** (12 g, 38 mmol) and benzylamine (3.9 g, 36 mmol) were transformed into amide $L^4$ (4.9 g, 35%);

**Table 3** Positional parameters and their estimated standard deviations (e.s.d.s)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Complex **1** | | | | | | | |
| C(1) | 0.319 2(4) | −0.000 0(2) | 0.385 7(3) | C(26) | 0.373 7(6) | −0.047 8(4) | 0.157 8(4) |
| C(2) | 0.248 3(4) | −0.046 2(3) | 0.423 9(3) | C(27) | 0.184 3(6) | −0.037 4(4) | 0.082 4(4) |
| C(3) | 0.143 7(4) | −0.018 1(3) | 0.434 8(3) | C(28) | 0.406 6(4) | 0.169 8(3) | 0.583 3(3) |
| C(4) | 0.109 7(4) | 0.054 1(3) | 0.406 4(3) | Cu | 0.400 22(4) | 0.141 56(3) | 0.317 00(3) |
| C(5) | 0.183 1(3) | 0.097 8(2) | 0.369 0(2) | F(1) | 0.470 9(3) | 0.166 9(2) | 0.658 8(2) |
| C(6) | 0.147 9(3) | 0.175 2(3) | 0.331 5(3) | F(2) | 0.303 8(3) | 0.190 1(3) | 0.590 6(3) |
| C(7) | 0.160 2(3) | 0.177 4(3) | 0.239 7(3) | F(3) | 0.399 5(3) | 0.097 7(2) | 0.555 8(2) |
| C(8) | 0.300 9(4) | 0.277 0(3) | 0.232 0(3) | F(4) | −0.247 7(5) | 0.114 3(3) | 0.182 5(3) |
| C(9) | 0.412 5(4) | 0.305 4(3) | 0.207 1(3) | F(5) | −0.078 9(3) | 0.088 6(3) | 0.225 7(3) |
| C(10) | 0.521 3(4) | 0.269 7(2) | 0.253 0(3) | F(6) | −0.186 3(6) | 0.015 1(3) | 0.147 7(3) |
| C(11) | 0.729 4(4) | 0.286 9(3) | 0.302 9(3) | N(2) | 0.281 0(3) | 0.191 4(2) | 0.227 0(2) |
| C(12) | 0.739 8(4) | 0.313 8(4) | 0.392 7(3) | N(4) | 0.288 4(3) | 0.072 1(2) | 0.359 2(2) |
| C(13) | 0.859 8(4) | 0.306 7(3) | 0.442 2(3) | N(5) | 0.617 0(3) | 0.309 1(2) | 0.255 6(2) |
| C(14) | 0.909 3(4) | 0.235 2(3) | 0.466 3(3) | O(1) | 0.394 3(3) | 0.223 5(2) | 0.434 1(2) |
| C(15) | 1.018 5(5) | 0.230 5(3) | 0.513 1(3) | O(2) | 0.582 0(3) | 0.194 8(2) | 0.514 1(2) |
| C(16) | 1.079 7(4) | 0.296 6(4) | 0.538 7(3) | O(3) | 0.476 3(4) | 0.304 7(2) | 0.551 2(2) |
| C(17) | 0.923 7(4) | 0.372 1(3) | 0.466 4(3) | O(4) | −0.207 5(5) | 0.074 3(2) | 0.360 4(3) |
| C(18) | −0.175 0(5) | 0.058 9(3) | 0.210 9(4) | O(5) | −0.134 6(3) | −0.044 2(2) | 0.322 3(3) |
| C(19) | 1.032 5(5) | 0.367 0(4) | 0.515 9(4) | O(6) | −0.330 9(4) | −0.011 6(4) | 0.272 5(4) |
| C(21) | 0.294 4(4) | 0.163 2(2) | 0.141 3(2) | O(7) | 0.522 9(2) | 0.204 6(2) | 0.286 2(2) |
| C(22) | 0.286 2(4) | 0.076 6(3) | 0.133 8(3) | O(8) | 0.532 4(2) | 0.083 6(2) | 0.385 3(2) |
| C(23) | 0.380 9(5) | 0.031 8(3) | 0.166 5(3) | S(1) | 0.471 9(1) | 0.230 69(7) | 0.513 39(7) |
| C(24) | 0.185 9(5) | 0.042 8(3) | 0.091 4(3) | S(2) | −0.218 1(1) | 0.013 95(8) | 0.300 44(9) |
| C(25) | 0.276 2(7) | −0.080 9(3) | 0.116 4(4) | | | | |
| Complex **2** | | | | | | | |
| C(1) | 0.129(1) | 0.265(2) | 0.027(1) | C(27) | 0.333(2) | 0.710(2) | 0.204(2) |
| C(2) | 0.008(2) | 0.278(1) | 0.020(1) | C(28) | −0.410(1) | 0.090(2) | 0.136(2) |
| C(3) | −0.025(1) | 0.349(1) | 0.136(1) | Cu | 0.165 8(2) | 0.341 7(2) | 0.289 6(2) |
| C(4) | −0.133(1) | 0.479(2) | 0.241(2) | F(1) | 0.394(1) | 0.648(1) | 0.136(1) |
| C(5) | −0.304(2) | 0.518(2) | 0.155(2) | F(2) | 0.395(1) | 0.769(1) | 0.307(1) |
| C(6) | −0.369(2) | 0.592(2) | 0.139(2) | F(3) | 0.313(1) | 0.784 8(9) | 0.153(1) |
| C(7) | −0.329(2) | 0.707(2) | 0.186(2) | F(4) | −0.467 6(8) | 0.065(1) | 0.235(1) |
| C(7) | −0.225(2) | 0.754(2) | 0.248(2) | F(5) | −0.440 4 | 0.001 9 | 0.037 9 |
| C(9) | −0.158(2) | 0.675(2) | 0.262(2) | F(6) | −0.430 0 | 0.183 5 | 0.116 9 |
| C(10) | −0.200(1) | 0.557(1) | 0.217(1) | N(1) | 0.172(1) | 0.227(1) | 0.124(1) |
| C(11) | 0.101(2) | 0.109(1) | 0.119(2) | N(3) | 0.316(1) | 0.339(1) | 0.361(1) |
| C(12) | 0.121(2) | 0.079(1) | 0.234(2) | N(4) | −0.099(1) | 0.410(1) | 0.131(1) |
| C(13) | 0.202(2) | 0.014(2) | 0.243(2) | O(1) | −0.216(2) | 0.097(2) | 0.091(2) |
| C(14) | 0.219(2) | −0.004(2) | 0.347(2) | O(2) | 0.017 4(9) | 0.352(1) | 0.238 2(8) |
| C(15) | 0.166(3) | 0.038(2) | 0.444(2) | O(3) | −0.248(2) | 0.214(2) | 0.286(2) |
| C(16) | 0.085(2) | 0.098(2) | 0.435(2) | O(4) | 0.148(1) | 0.558(1) | 0.103(1) |
| C(17) | 0.069(2) | 0.117(2) | 0.327(2) | O(5) | 0.150(1) | 0.692(1) | 0.300(1) |
| C(18) | 0.289(1) | 0.217(2) | 0.105(1) | O(6) | 0.245(1) | 0.534(1) | 0.278(1) |
| C(19) | 0.378(1) | 0.331(1) | 0.165(1) | O(7) | −0.265(8) | 0.009(4) | 0.263(5) |
| C(20) | 0.402(1) | 0.352(1) | 0.295(1) | O(8) | 0.126 0(8) | 0.421 7(9) | 0.454 4(9) |
| C(21) | 0.510(1) | 0.340(2) | 0.346(2) | O(9) | 0.102(1) | 0.648(1) | 0.516(1) |
| C(22) | 0.527(2) | 0.341(2) | 0.462(2) | S(1) | 0.205 2(4) | 0.613 7(4) | 0.222 7(4) |
| C(23) | 0.437(2) | 0.344(2) | 0.529(2) | S(2) | −0.266 3(6) | 0.115 7(8) | 0.190 3(7) |
| C(24) | 0.330(1) | 0.339(1) | 0.472(1) | | | | |
| Complex **3** | | | | | | | |
| C(1) | 0.325 1(4) | −0.001 0(3) | 0.388 7(3) | C(26) | 0.352 8(5) | −0.054 0(3) | 0.152 9(3) |
| C(2) | 0.254 8(5) | −0.048 7(3) | 0.424 6(3) | C(27) | 0.168 7(5) | −0.032 8(3) | 0.067 2(4) |
| C(3) | 0.146 7(5) | −0.022 4(3) | 0.435 9(4) | C(28) | 0.398 5(4) | 0.170 5(3) | 0.593 8(3) |
| C(4) | 0.110 5(4) | 0.049 5(3) | 0.409 5(3) | Cu | 0.404 07(5) | 0.140 80(3) | 0.319 21(4) |
| C(5) | 0.185 2(4) | 0.095 4(3) | 0.372 8(3) | F(1) | 0.464 5(3) | 0.167 6(2) | 0.667 1(2) |
| C(6) | 0.147 7(4) | 0.172 8(3) | 0.337 0(3) | F(2) | 0.294 1(3) | 0.187 9(3) | 0.604 5(3) |
| C(7) | 0.158 6(4) | 0.174 1(3) | 0.245 8(3) | F(3) | 0.394 8(3) | 0.099 1(2) | 0.564 8(2) |
| C(8) | 0.297 7(4) | 0.275 2(3) | 0.234 9(3) | F(4) | −0.260 1(4) | 0.114 2(3) | 0.181 2(3) |
| C(9) | 0.408 7(4) | 0.305 6(3) | 0.209 9(3) | F(5) | −0.088 6(3) | 0.105 0(3) | 0.239 3(3) |
| C(10) | 0.519 9(4) | 0.274 7(3) | 0.258 3(3) | F(6) | −0.159 2(5) | 0.019 8(3) | 0.155 7(3) |
| C(11) | 0.728 9(4) | 0.294 6(3) | 0.306 9(3) | N(2) | 0.281 2(3) | 0.189 5(2) | 0.231 7(2) |
| C(12) | 0.732 2(5) | 0.318 5(4) | 0.395 8(4) | N(4) | 0.291 9(3) | 0.070 8(2) | 0.362 9(2) |
| C(13) | 0.853 4(4) | 0.310 2(3) | 0.445 3(3) | N(5) | 0.615 0(4) | 0.315 4(3) | 0.258 0(3) |
| C(14) | 0.901 1(5) | 0.238 8(3) | 0.466 3(3) | O(1) | 0.382 6(3) | 0.228 7(2) | 0.448 6(2) |
| C(15) | 1.011 5(5) | 0.233 1(4) | 0.512 7(4) | O(2) | 0.573 6(3) | 0.203 2(2) | 0.525 8(2) |
| C(16) | 1.074 8(5) | 0.298 3(4) | 0.538 1(4) | O(3) | 0.460 1(4) | 0.309 0(2) | 0.565 3(2) |
| C(17) | 0.918 3(5) | 0.375 7(3) | 0.470 2(3) | O(4) | −0.248 0(3) | 0.071 5(2) | 0.353 1(2) |
| C(18) | −0.179 7(5) | 0.064 1(4) | 0.213 5(4) | O(5) | −0.138 6(3) | −0.040 2(2) | 0.323 0(3) |
| C(19) | 1.026 1(5) | 0.369 1(4) | 0.517 5(4) | O(6) | −0.337 1(3) | −0.023 8(2) | 0.254 7(3) |
| C(21) | 0.292 2(4) | 0.160 9(3) | 0.147 1(3) | O(7) | 0.524 0(3) | 0.213 0(2) | 0.297 3(2) |

**Table 2** (*continued*)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Complex 3 | | | | | | | |
| C(22) | 0.276 0(4) | 0.075 1(3) | 0.135 5(3) | O(8) | 0.536 8(3) | 0.095 0(2) | 0.400 6(2) |
| C(23) | 0.362 6(4) | 0.024 0(3) | 0.169 6(3) | O(9) | 0.457 3(3) | 0.055 0(2) | 0.221 1(2) |
| C(24) | 0.177 7(4) | 0.045 8(3) | 0.084 0(3) | S(1) | 0.459 6(1) | 0.236 27(8) | 0.526 10(8) |
| C(25) | 0.256 3(5) | −0.081 6(3) | 0.101 1(4) | S(2) | −0.231 1(1) | 0.012 38(8) | 0.295 34(9) |
| Complex 4 | | | | | | | |
| C(1) | 0.746(2) | 0.446(2) | 0.305(3) | C(26) | 0.674(3) | 0.065(3) | 0.589(4) |
| C(2) | 0.813(2) | 0.507(2) | 0.445(3) | C(27) | 1.055(3) | 0.837(2) | 0.586(3) |
| C(3) | 0.821(2) | 0.445(2) | 0.525(3) | C(28) | 0.705(4) | 0.787(4) | 0.251(5) |
| C(4) | 0.917(2) | 0.432(2) | 0.720(3) | Cu | 0.631 6(3) | 0.267 5(3) | 0.351 6(4) |
| C(5) | 1.054(2) | 0.587(2) | 0.896(3) | F(1) | 0.903(2) | 0.061(2) | 0.350(2) |
| C(6) | 1.158(3) | 0.630(2) | 0.997(3) | F(2) | 1.054(2) | 0.171(2) | 0.421(2) |
| C(7) | 1.221(3) | 0.568(2) | 1.015(3) | F(3) | 0.926(2) | 0.197(2) | 0.510(2) |
| C(8) | 1.197(3) | 0.473(2) | 0.949(3) | F(4) | 0.678(3) | 0.754(3) | 0.150(3) |
| C(9) | 1.094(2) | 0.420(2) | 0.848(3) | F(5) | 0.274(2) | 0.290(2) | 0.689(3) |
| C(10) | 1.027(2) | 0.483(2) | 0.827(3) | F(6) | 0.242(3) | 0.138(2) | 0.653(3) |
| C(11) | 0.569(2) | 0.457(2) | 0.346(3) | N(1) | 0.627(1) | 0.384(1) | 0.286(2) |
| C(12) | 0.448(2) | 0.407(2) | 0.322(3) | N(2) | 0.642(2) | 0.164(2) | 0.435(2) |
| C(13) | 0.367(2) | 0.428(2) | 0.241(3) | N(3) | 0.510(2) | 0.157(1) | 0.200(2) |
| C(14) | 0.253(2) | 0.377(2) | 0.220(3) | N(4) | 0.908(2) | 0.486(1) | 0.633(2) |
| C(15) | 0.224(2) | 0.311(2) | 0.272(3) | O(1) | 0.500(1) | 0.317(1) | 0.456(2) |
| C(16) | 0.304(2) | 0.290(2) | 0.354(3) | O(2) | 0.750(1) | 0.360(1) | 0.504(2) |
| C(17) | 0.419(2) | 0.336(2) | 0.373(3) | O(4) | 0.957(1) | 0.330(1) | 0.359(2) |
| C(18) | 0.575(2) | 0.342(2) | 0.140(3) | O(5) | 0.782(1) | 0.197(1) | 0.272(2) |
| C(19) | 0.584(2) | 0.236(2) | 0.072(3) | O(6) | 0.933(2) | 0.173(1) | 0.181(2) |
| C(20) | 0.505(2) | 0.157(2) | 0.086(3) | O(7) | 0.529(2) | 0.856(2) | 0.272(3) |
| C(21) | 0.417(2) | 0.081(2) | −0.022(3) | O(8) | 0.502(3) | 0.328(3) | 0.773(3) |
| C(22) | 0.341(2) | 0.013(2) | 0.005(3) | O(9) | 0.579(2) | 0.803(2) | 0.436(3) |
| C(23) | 0.344(2) | 0.015(2) | 0.122(3) | S | 1.100 3(6) | 0.779 6(5) | 0.710 2(8) |
| C(24) | 0.434(2) | 0.093(2) | 0.226(3) | S(1) | 0.556 9(8) | 0.776 0(1) | 0.301(1) |
| C(25) | 0.656(3) | 0.123(2) | 0.499(3) | | | | |

$\nu_{max}$(neat) 3410 (OH), 3300 (NH), 1650 (C=O), 1580 (C=N) and 1510 $cm^{-1}$ (C=C); NMR ($CDCl_3$, standard $SiMe_4$): $^1H$(200 MHz), δ 8.42 (1 H, d, *J* 4.8, CH of $C_5H_4N$), 7.56 (1 H, t, *J* 7.6, CH of $C_5H_4N$), 7.57–7.04 (9 H, m, $C_6H_5$, 2 CH of $C_5H_4N$, CH of $C_6H_4OH$ and OH), 6.95 (1 H, dd, *J* 7.9, 1.7, CH of $C_6H_4OH$), 6.79 (d, *J* 8, CH of $C_6H_4OH$), 6.77 (1 H, t, *J* 7.2, CH of $C_6H_4OH$), 6.60 (1 H, br s, CONH), 4.25 (2 H, d, *J* 5.7, $C_6H_5CH_2NHCO$), 3.80 (2 H, s, $C_6H_5CH_2N$), 3.05 (4 H, m, $C_5H_4NCH_2CH_2N$), 2.96 (2 H, t, *J* 7 Hz, $NCH_2CONH$) and 2.40 (2 H, t, *J* 7 Hz, $NCH_2CH_2CONH$); $^{13}C$(50 MHz), δ 171.39 (C=O), 159.31 (C), 157.48 (C), 148.90 (CH), 138.56 (C), 136.51 (CH), 128.96 (CH), 128.65 (CH), 128.37 (2 CH), 127.54 (CH), 127.31 (CH), 127.00 (CH), 123.32 (CH), 122.09 (C), 121.36 (CH), 119.07 (CH), 116.01 (CH), 58.41 ($CH_2$), 52.90 ($CH_2$), 49.47 ($CH_2$), 43.06 ($CH_2$), 34.54 ($CH_2$) and 33.03 ($CH_2$).

$[CuL^1(H_2O)][CF_3SO_3]_2$ **1**. To anhydrous tetrahydrofuran (2 $cm^3$) were added amide $L^1$ (310 mg, 0.8 mmol) and $Cu(CF_3SO_3)_2$ (290 mg, 0.8 mmol). The mixture was allowed to stand at room temperature for 1 h. Evaporation of tetrahydrofuran afforded complex **1** (550 mg, 89%) (Found: C, 42.30; H, 4.10; N, 5.45. $C_{27}H_{31}CuF_6N_3O_8S_2$ requires C, 42.25; H, 4.05; N, 5.50%); $\nu_{max}$(KBr) 3378 and 3131 (NH), 1623 (C=O), 1490 (C=N), 1455 (C=C), 1297, 1222 and 1023 $cm^{-1}$; $\lambda_{max}$/nm(MeCN) 656 (ε/$dm^3$ $mol^{-1}$ $cm^{-1}$ 112).

$[CuL^2(H_2O)][CF_3SO_3]_2 \cdot H_2O$ **2**. By a procedure analogous to the synthesis of complex **1**, amide $L^2$ (110 mg, 290 mmol) and $Cu(CF_3SO_3)_2$ (130 mg, 350 mmol) in anhydrous thf (2 $cm^3$) were transformed into complex **2** (150 mg, 51%) (Found: C, 40.50; H, 4.05; N, 5.40. $C_{26}H_{31}CuF_6N_3O_9S_2$ requires C, 40.50; H, 4.05; N, 5.45); $\nu_{max}$(KBr) 3322 (NH), 1609 (C=O), 1578 (C=N) and 1243 $cm^{-1}$; $\lambda_{max}$/nm(MeCN) 659 (ε/$dm^3$ $mol^{-1}$ $cm^{-1}$ 97).

$[CuL^3(H_2O)][CF_3SO_3]_2$ **3**. By a procedure analogous to the synthesis of complex **1**, amide $L^3$ (270 mg, 0.67 mmol) and $Cu(CF_3SO_3)_2$ (240 mg, 0.67 mmol) in anhydrous thf (2 $cm^3$) were transformed into complex **3** (400 mg, 75%) (Found: C, 41.45; H, 4.00; N, 5.40. $C_{27}H_{31}CuF_6N_3O_9S_2$ requires C, 41.40; H, 4.00; N, 5.35%); $\lambda_{max}$/nm(MeCN) 650 (ε/$dm^3$ $mol^{-1}$ $cm^{-1}$ 182) and 415 (2087).

$[CuL^4(MeCN)][CF_3SO_3]_2$ **4**. By a procedure analogous to the synthesis of complex **1**, amide $L^4$ (1.33 g, 3.4 mmol) and $Cu(CF_3SO_3)_2$ (1.24 g, 3.4 mmol) in anhydrous thf (5 $cm^3$) were transformed into complex **4** (1.3 g, 52%) (Found: C, 42.40; H, 3.85; N, 7.00. $C_{28}H_{30}CuF_6N_4O_8S_2$ requires C, 42.45; H, 3.80; N, 7.05%); $\nu_{max}$(KBr) 3439 (OH), 3378 (NH), 1614 (C=O), 1515 (C=N), 1490 and 1462 (C=C) and 1285 $cm^{-1}$; $\lambda_{max}$/nm(MeCN) 641 (ε/$dm^3$ $mol^{-1}$ $cm^{-1}$ 86) and 421 (2166).

(*c*) *Crystal Structure Determinations*.—The crystals were obtained by crystallization at 4 °C of saturated acetonitrile solutions of the copper complexes **1**–**4** using diethyl ether vapour diffusion. The dark blue moisture-sensitive tablets were sealed in Lindemann glass capillaries under a stream of dry $N_2$.

*Crystal data*. Crystal data together with details of the X-ray diffraction experiments are in Table 1.

*Data collection and processing*. Enraf-Nonius CAD-4 diffractometer, ω–2θ mode, temperature 20 °C, monochromated Mo-Kα (λ = 0.710 73 Å) radiation. Cell constants and the orientation matrix for data collection were obtained from least-squares refinement, using setting angles of 25 reflections in the range $20 < 2\theta < 32°$. Three intense reflections were recorded throughout the data collection every $10^3$ s and showed no change in intensity for crystals **1**–**3** but a 14% loss of intensity for **4**. Owing to the poor quality of crystal **4** only 2732 reflections were measured and a linear decay correction was applied; 1602 with $I > 3\sigma(I)$ were kept for the structure determination compared to 3376 for crystal **1**, 3030 for **2** and 2827 for **3**. Lorentz and polarization corrections were applied to the raw data; absorption corrections were not necessary (see Table 1).

*Structure analysis and refinement*. The structures were solved by the Patterson method and MULTAN[17] calculations. The remaining non-hydrogen atoms were located in successive

**Table 3** Selected bond distances (Å) and angles (°) with e.s.d.s

| | | | |
|---|---|---|---|
| Complex **1** | | | |
| Cu–O(1) | 2.386(3) | Cu–N(2) | 2.032(3) |
| Cu–O(7) | 1.942(3) | Cu–N(4) | 1.989(3) |
| Cu–O(8) | 2.012(3) | | |
| O(7)–Cu–N(2) | 91.2(1) | O(7)–Cu–O(8) | 83.8(1) |
| O(7)–Cu–N(4) | 173.3(1) | O(7)–Cu–O(1) | 89.6(1) |
| N(2)–Cu–O(8) | 167.7(1) | N(2)–Cu–N(4) | 95.5(1) |
| N(2)–Cu–O(1) | 101.9(1) | O(8)–Cu–N(4) | 89.8(1) |
| O(8)–Cu–O(1) | 89.2(1) | N(4)–Cu–O(1) | 88.7(1) |
| Complex **2** | | | |
| Cu–O(2) | 1.93(1) | Cu–N(1) | 2.05(1) |
| Cu–O(6) | 2.40(1) | Cu–N(3) | 1.99(1) |
| Cu–O(8) | 2.04(1) | | |
| O(2)–Cu–N(1) | 90.9(5) | O(2)–Cu–O(6) | 90.1(5) |
| O(6)–Cu–N(1) | 105.5(5) | O(2)–Cu–O(8) | 82.5(4) |
| N(1)–Cu–O(8) | 164.5(2) | N(1)–Cu–N(3) | 95.3(5) |
| N(3)–Cu–O(6) | 89.7(5) | O(2)–Cu–N(3) | 173.6(5) |
| O(6)–Cu–O(8) | 87.6(4) | N(3)–Cu–O(8) | 91.2(5) |
| Complex **3** | | | |
| Cu–O(7) | 1.947(3) | Cu–N(2) | 2.040(3) |
| Cu–O(8) | 2.033(3) | Cu–N(4) | 1.993(4) |
| Cu–O(9) | 2.346(3) | | |
| O(7)–Cu–N(2) | 92.4(1) | O(7)–Cu–O(8) | 83.4(1) |
| O(7)–Cu–N(4) | 169.7(1) | O(7)–Cu–O(9) | 90.6(1) |
| N(2)–Cu–O(8) | 175.2(1) | N(2)–Cu–N(4) | 94.8(1) |
| N(2)–Cu–O(9) | 90.5(1) | O(8)–Cu–N(4) | 89.6(1) |
| O(8)–Cu–O(9) | 87.1(1) | N(4)–Cu–O(9) | 96.7(1) |
| Complex **4** | | | |
| Cu–O(1) | 2.38(2) | Cu–N(2) | 2.00(3) |
| Cu–O(2) | 1.93(1) | Cu–N(3) | 2.02(2) |
| | | Cu–N(1) | 2.02(2) |
| O(1)–Cu–O(2) | 89.7(7) | O(1)–Cu–N(2) | 88.1(9) |
| O(1)–Cu–N(3) | 91.0(8) | O(1)–Cu–N(1) | 89.2(8) |
| O(2)–Cu–N(2) | 83.1(8) | O(2)–Cu–N(3) | 173.4(9) |
| O(2)–Cu–N(1) | 91.6(8) | N(2)–Cu–N(3) | 90.4(9) |
| N(2)–Cu–N(1) | 174.0(8) | N(3)–Cu–N(1) | 95.0(9) |

Fourier difference syntheses. Hydrogen atoms found in the Fourier difference syntheses or at idealized positions were included in the structure-factor calculation but not refined. Scattering factors were taken from Cromer and Waber.[18a] Anomalous dispersion effects were included in $F_c$; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[18b]

In the final cycles of refinement, all non-hydrogen atoms were refined anisotropically for compounds **1** and **3**. The crystal structure of **2** could not be refined properly owing to the disorder observed in one triflate anion. Atom O(7) and the $CF_3$ moiety were fixed in average positions. However the quality of the structure determination is quite acceptable, thus it was possible to locate the hydrogen atoms of the water molecules in the Fourier difference maps. For compound **4** only six atoms (Cu and the five co-ordinated atoms) were refined anisotropically. The largest peaks in the final difference maps were located near the Cu atoms.

All the calculations were performed on a microVAX computer using SDP software.[19] The final atomic coordinates are in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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