Heteroleptic Tripodal Complexes of Copper(II): Towards a Synthetic Model for the Active Site in Galactose Oxidase†

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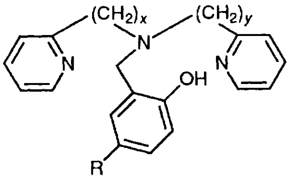
A series of copper(II) complexes derived from tripodal ligands (HL) bearing pyridyl and phenolic arms have been synthesized and characterized. The molecular structures of complexes $[CuL^4(O_2CMe)]\cdot H_2O$ and $[CuL^4(SCN)]\cdot MeCO_2Et$ {HL^4 = 2-bis[2-(2-pyridyl)ethyl]aminomethyl-4-nitrophenol} were determined by X-ray diffraction; the complexes exist as neutral, mononuclear species in the solid state. The co-ordination geometry around the copper atom in each is a distorted square-based pyramid (τ = 0.08 and 0.11) where one pyridyl nitrogen occupies the axial position ($Cu-N_{py}$ 2.27 and 2.20 Å). Three ligand donor atoms comprising the square plane are unchanged but the fourth ligand is an exogenous donor atom from $MeCO_2^-$ or SCN^- respectively. Reference is made to the relationship of the structures to that found at the copper(II) centre at the active site of galactose oxidase.

Galactose oxidase (GOase) is an extracellular metalloenzyme secreted by the fungus *Dactylium dendroides*. It catalyses the stereospecific oxidation of a broad range of primary alcohol substrates and possesses a unique mononuclear copper site which catalyses a two-electron-transfer reaction during the oxidation of primary alcohols to the corresponding aldehydes.[1–3] The active site in GOase has been shown, by X-ray crystal structural analysis at 1.7 Å resolution,[4] to be quite distinct from those in copper-containing enzymes such as ascorbate oxidase and superoxide dismutase. At pH 4.5, consistent with spectroscopic features, the copper has a square-pyramidal co-ordination environment with an almost perfect square plane consisting of two histidine nitrogen atoms (His-496 and His-581), a tyrosine phenoxide oxygen (Tyr-272), and an oxygen atom from an exogenous acetate anion. At pH 7.0 the copper site has essentially the same structure but the acetate has been replaced by a water molecule; at a distance of 2.8 Å from the metal, this molecule is probably not co-ordinated so that the site is best described as distorted tetrahedral with only the four protein residues attached to the metal. Until recently only a limited number of investigations have considered complexes which might structurally model the metal site in GOase.[5–9] Uma *et al.*[6] have reported a series of mononuclear copper(II) complexes derived from tripodal ligands bearing phenolate, benzimidazolate and/or pyridine pendants; the X-ray structural analysis of one of their complexes revealed the presence of an axial copper(II)–phenolate bond which was considered to mimic the axial copper(II)–phenolate bond in the enzyme. In parallel with studies concerning the physical and chemical analysis of GOase,[10–12] Whittaker *et al.*[8] investigated the structures of several monocopper(II) complexes derived from the simple polyamine *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine and *p*-cresol, 2-methylsulfanyl- or 2-methylsulfinyl-*p*-cresol in order to gain insight into the co-ordination chemistry associated with the assignment of the protein radical to a novel tyrosine–cysteine covalent cross-link structure.[4]

We have used a series of tripodal compounds bearing pyridyl and phenolic arms in a programme designed to search for small molecular models for the GOase site.[9] In the absence of an exogenous donor or in the presence of only weakly co-ordinating anions, such as perchlorate, these compounds form dimeric copper(II) complexes in which two copper(II) atoms share two phenolic oxygens from two ligands. In order to inhibit dimer formation and thus prepare the related mononuclear copper(II) complexes, more strongly co-ordinating anions than perchlorate and tetrafluoroborate have been introduced into the copper(II) co-ordination sphere. For example the acetate anion has been used in order to simulate the basal interaction found at the copper(II) site in GOase.



R = H:
x = 1, y = 2 HL^1
x = y = 2 HL^2
R = NO_2:
x = 1, y = 2 HL^3
x = y = 2 HL^4
x = y = 1 HL^5

Experimental

Reagents and solvents used were of commercial reagent quality. Purification of the pro-ligands was effected by flash chromatography with silica gel (40–63 µm).[10] The identity and purity of each was judged by TLC, ^1H NMR, and mass spectrometry. All elemental analyses were carried out by the University of Sheffield Microanalytical Service. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 1710 IR Fourier-transform spectrophotometer (4000–400 cm^{-1}), electronic absorption spectra using a Philips PU8720 UV/VIS scanning spectrophotometer operating in the range 220–880 nm, ^1H NMR spectra at 220 MHz on a Perkin-Elmer R34 spectrometer, ^{13}C NMR spectra (62.9 MHz) using a Bruker AM-250 spectrometer and positive-ion fast atom bombardment (FAB) mass spectra on a Kratos MS 80 spectrometer using a 3-nitrobenzyl alcohol matrix unless otherwise stated.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

CAUTION: Although no problems were encountered during the preparation of the perchlorate salts described below, suitable care and precautions should be taken when handling such potentially hazardous compounds.

Pro-ligand Synthesis.—Di[2-(2-pyridyl)ethyl]amine, and *o*-acetoxybenzyl bromide were synthesised according to literature procedures.[13,14]

[2-(2-Pyridyl)ethyl](2-pyridylmethyl)amine. 5 mol dm^{-3} Sodium hydroxide (4 cm^3, 20 mmol) was added to (chloromethyl)pyridine hydrochloride (3.3 g, 20 mmol) dissolved in ice–water (15 cm^3). The ensuing red solution was added dropwise to a stirred ice–water solution containing 2-(2-aminoethyl)pyridine (2.45 g, 20 mmol). The clear yellow solution was allowed to warm to 60 °C, changing to orange. 5 mol dm^{-3} Sodium hydroxide (4 cm^3) was added in portions during 1 d. After cooling, the resultant mixture was extracted with dichloromethane (2 × 50 cm^3). The extracted solution was dried with $MgSO_4$, and evaporated to remove the solvent. A red-brown crude oil was recovered; vacuum distillation of the oil yielded 2.2 g of pure product (51.6%). NMR ($CDCl_3$): ^1H, δ 2.22 (s, 1 H, NH), 3.00 [m, 4 H, $(CH_2)_2$], 3.85 (s, 2 H, CH_2), 7.00–7.55 (m, 6 H, aryl) and 8.45 (d, 2 H, pyridine); ^{13}C, δ 37.1, 49.1, 54.8, 121.2, 121.6, 121.8, 123.4, 136.4, 136.6, 149.2, 149.3, 159.9 and 160.2.

The pro-ligands HL^1 and HL^2 were prepared by the method of Karlin *et al.*;[15] HL^3 and HL^4 were prepared in a similar way and a representative procedure is described. A tetrahydrofuran (100 cm^3) solution containing [2-(2-pyridyl)ethyl](2-pyridylmethyl)amine (2.13 g, 10 mmol), or di[2-(2-pyridyl)ethyl]amine (2.27 g), and triethylamine (20 mmol, 2.02 g) was stirred in an ice-bath. To it, 2-chloromethyl-4-nitrophenol (10 mmol, 1.88 g) in tetrahydrofuran (50 cm^3) was added dropwise while stirring the solution rapidly. The solution was then allowed to warm to room temperature with some accompanying precipitation of triethylamine hydrochloride. The mixture was then heated to reflux for 2 h. After cooling, the suspension was filtered and the solvent evaporated. The resultant crude oil was chromatographed with CH_2Cl_2–MeOH (9:1) to generate the pure pro-ligands HL^3 (2.45 g, 67.2%) and HL^4 (2.74 g, 72.3%). Spectroscopic data for the new pro-ligands: HL^1, ^1H NMR ($CDCl_3$) δ 2.95 [m, 4 H, $(CH_2)_2$], 3.80 (d, 2 H, CH_2), 6.70–7.60 (m, 10 H, aryl), 8.45 and 8.55 (2 d, 2 H, pyridine); ^{13}C NMR ($CDCl_3$) δ 35.2, 53.6, 57.4, 59.3, 116.3, 119.1, 121.4, 122.2, 122.3, 122.8, 123.2, 128.9, 129.3, 136.5, 136.8, 149.1, 149.2, 157.6, 158.2 and 159.6; mass spectrum: m/z = 320 (M^+, 100), 227 (90), 212 (45) and 121 (74%); HL^3, ^1H NMR ($CDCl_3$) δ 2.95 [m, 4 H, $(CH_2)_2$], 3.75 (s, 2 H, CH_2), 3.85 (s, 2 H, CH_2), 6.70–8.05 (m, 9 H, aryl), 8.35 and 8.45 (2 d, 2 H, pyridine); ^{13}C NMR ($CDCl_3$) δ 35.2, 53.3, 56.5, 58.6, 116.8, 121.5, 122.6, 123.0, 123.2, 125.4, 125.8, 136.5, 137.0, 139.8, 148.9, 149.2, 157.0, 159.3 and 164.3; mass spectrum: m/z = 365 (M^+, 80), 272 (95), 212 (90) and 121 (100%); HL^4, ^1H NMR ($CDCl_3$) δ 3.05 [m, 8 H, $(CH_2)_2$], 3.90 (s, 2 H, CH_2), 6.75–8.05 (m, 9 H, aryl), 8.45 (2 d, 2 H, pyridine) and 9.90 (s, 1 H, OH); ^{13}C NMR ($CDCl_3$) δ 34.6, 53.0, 57.3, 116.5, 121.6, 122.1, 123.3, 124.9, 125.3, 136.6, 140.0, 149.4, 158.9 and 164.5; mass spectrum: m/z = 379 (M^+, 100), 286 (78), 274 (45), 228 (49), 114 (85), 106 (40) and 94 (10%).

Metal Complexation Reactions.—$[(CuL^1)_2][ClO_4]_2 \cdot H_2O$ **1**. The salt $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol) in methanol (4 cm^3) was added to a methanolic solution containing pro-ligand HL^1 (1 mmol, 25 cm^3). Triethylamine (1 mmol) was added and the clear green solution heated to reflux for 2 h. On cooling, the mixture was filtered to remove residual solids. The filtrate was allowed to stand at room temperature for a few days during which time a green precipitate developed. The solid was recrystallized from MeOH–MeCN. Yield 0.27 g (55.8%).

$[CuL^1(O_2CCMe_3)] \cdot H_2O$ **2**. The compound $Cu(O_2CCMe_3)_2$ (0.27 g, 1 mmol), in methanol (4 cm^3) was added to a methanolic solution (50 cm^3) containing pro-ligand HL^1 (0.32 g, 1 mmol); triethylamine (1 mmol) was added and the clear green solution was heated to reflux for 1 h. The resultant mixture was allowed to stand at room temperature for several days and then the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane (5 cm^3), then diethyl ether (≈20 cm^3) was added dropwise. The solution was allowed to stand at −20 °C overnight and blue crystals were collected (0.31 g, 64.2%).

$[(CuL^2)_2][ClO_4]_2 \cdot H_2O$ **3**. Pro-ligand HL^2 (0.34 g, 1 mmol) and triethylamine (1 mmol) were dissolved in methanol (30 cm^3). The salt $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol) in methanol (5 cm^3) was added to the yellow solution which then turned brown. The mixture was heated at reflux for 4 h. After cooling, the resulting solution was filtered to remove residual solids. Dark green crystals were obtained either by leaving the filtrate to stand at room temperature for 3 d or by using diethyl ether vapour-diffusion techniques. Yield 0.36 g (72.3%).

$[(CuL^2)_2][CF_3SO_3]_2$ **4**. A solution of $Cu(O_3SCF_3)_2$ (1 mmol, 0.36 g) in ethanol (5 cm^3) was added to an ethanolic solution (25 cm^3) containing pro-ligand HL^2 (1 mmol) and triethylamine (1 mmol). The dark brown solution was heated to reflux for 1 h. On cooling, some solid precipitated and was filtered off. A further period of standing gave a black-brown crystalline solid (0.38 g, 69.4%).

$[CuL^2(Cl)] \cdot 2H_2O$ **5** *and* $[CuL^2(N_3)] \cdot H_2O$ **6**. These complexes were synthesized by the literature procedure.[15]

$[(CuL^3)_2][ClO_4]_2 \cdot 2H_2O$ **7**. The salt $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol) in methanol (5 cm^3) was added to a methanolic solution (30 cm^3) containing pro-ligand HL^3 (1 mmol, 0.36 g). The yellow solution turned to green and gave a green precipitate on addition of triethylamine (1 mmol). The suspension was heated to reflux for 1 h. After cooling, the resulting mixture was filtered to generate a green powder which was then recrystallized from MeCN–MeOH (1:4). Yield 0.23 g (42.6%).

$[(CuL^3)_2][BF_4]_2 \cdot 2H_2O$ **8**. Triethylamine (0.5 mmol) was added to a green methanolic solution (30 cm^3) containing pro-ligand HL^3 (1 mmol) and $Cu(BF_4)_2 \cdot H_2O$ (1 mmol, 0.12 g). There was an immediate green precipitation which redissolved when the suspension was heated to reflux. After refluxing for 2 h the resulting solution was filtered and the filtrate allowed to stand at room temperature overnight. A blue-green crystalline solid was collected (0.15 g, 55%).

$[CuL^3(Cl)] \cdot H_2O$ **9**. Copper(II) chloride (0.14 g, 1 mmol) in MeOH (5 cm^3) was added to a methanolic solution (30 cm^3) containing pro-ligand HL^3 (1 mmol). Triethylamine (1 mmol) was added and the mixture heated at reflux for 1 h. After cooling, the resulting mixture was filtered to remove residual solids. The filtrate was then evaporated to dryness. Methanol (5 cm^3) was added to dissolve the residue and then ethyl acetate (30 cm^3). This solution was allowed to stand at room temperature overnight. A green crystalline solid was collected, (0.34 g, 71.4%).

$[CuL^3(O_2CCMe_3)] \cdot H_2O$ **10**. This complex was synthesized by a procedure analogous to that of **9** using $Cu(O_2CCMe_3)_2$ (1 mmol) instead of $CuCl_2$. The resultant crude product was recrystallized from methanol–ethyl acetate (1:30), giving green-blue crystals (0.27 g, 53%).

$[(CuL^4)_2][ClO_4]_2 \cdot 2H_2O$ **11**. The salt $Cu(ClO_4)_2 \cdot 6H_2O$ (1.5 mmol) in MeOH (5 cm^3) was added to a methanolic solution (40 cm^3) containing pro-ligand HL^4 (0.38 g, 1 mmol) and triethylamine (1.5 mmol). The mixture was heated at reflux for 1.5 h. After cooling, the resulting solution was concentrated to 20 cm^3 and allowed to stand at 1 °C overnight. The yellow-green solid generated was filtered off and recrystallized using diethyl ether vapour diffusion in its MeOH–MeCN (4:1) solution to give small green crystals (0.41 g, 49.2%).

$[(CuL^4)_2][BF_4]_2 \cdot 2H_2O$ **12**. Triethylamine (1 mmol) was added to a methanolic solution (35 cm^3) containing pro-ligand HL^4 (1 mmol) and $Cu(BF_4)_2 \cdot H_2O$ (1 mmol). The mixture was stirred at room temperature for 4 h. The resulting suspension was filtered to give a fresh green powder, which was recrystallized from MeCN–MeOH (1 : 6). Yield 0.40 g (71%).

$[CuL^4(Cl)]\cdot 2H_2O$ **13**. Copper(II) chloride (1.5 mmol) in methanol (5 cm^3) was added to a methanolic solution (25 cm^3) containing pro-ligand HL^4 (1 mmol, 0.57 g) and triethylamine (1 mmol). A green precipitate emerged immediately and the mixture was heated at reflux with stirring for 1 h. After cooling the solid was filtered off and recrystallized from MeOH–MeCN (1 : 5). Yield 0.38 g (49%).

$[CuL^4(O_2CMe)]\cdot H_2O$ **14**. A solution of $Cu(O_2CMe)_2\cdot H_2O$ (1 mmol, 0.20 g) in hot EtOH (30 cm^3) was added dropwise to a solution of pro-ligand HL^4 (1 mmol, 0.38 g) in ethanol (30 cm^3). The mixture was adjusted to pH ≈ 8 with triethylamine then heated to reflux for 2 h. After cooling, the resulting solution was filtered to remove residual solid impurity. The filtrate was evaporated to near dryness and MeOH (5 cm^3) was added to dissolve the residue. Ethyl acetate (30 cm^3) was added and the solution was allowed to stand at room temperature for a few days until blue crystals developed (0.42 g, 81%).

$[CuL^4(SCN)]\cdot MeCO_2Et$ **15**. *Method A*. Complex **11** (0.58 g, 0.5 mmol) was dissolved in MeCN–MeOH (2 : 1, 20 cm^3). Sodium thiocyanate (1 mmol) in MeOH (5 cm^3) was added and the solution was then heated to reflux for 1 h. After cooling the solution was concentrated to about 5 cm^3 and ethyl acetate (25 cm^3) was added. Blue-green crystals were collected after leaving the solution to stand at room temperature overnight (0.43 g, 74%).

Method B. Complex **14** (0.26 g, 0.5 mmol) was dissolved in methanol (20 cm^3). To the green solution was added NaSCN (0.5 mmol) in MeOH (5 cm^3). The solution was heated at reflux for 1 h during which time it changed to brown-green. After cooling the resulting solution was evaporated to near dryness. Methanol (5 cm^3) was added to dissolve the residue then ethyl acetate (20 cm^3). The solution was allowed to stand overnight at room temperature and the resulting crystals collected (0.23 g, 77%).

All the complexes isolated were dried under vacuum over silica gel and $MgSO_4$ and their elemental analyses are recorded in Table 1.

Crystallography.—Crystal data and experimental conditions for complexes **14** and **15** are listed in Table 8.

Complex **14**. A crystal having dimensions of 0.60 × 0.55 × 0.40 mm was used to collect X-ray data at room temperature in the range $6.5 < 2\theta < 50.0°$ on a Stoe Stadi-2 diffractometer by the ω-scan method ($0 \leqslant h \leqslant 11, 0 \leqslant k \leqslant 11, -29 \leqslant l \leqslant 28$). The 4330 measured reflections yielded 3844 unique and 3240 independent reflections with $|F|/\sigma(|F|) > 4.0$; all data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved using the Patterson heavy-atom method, which revealed the position of the copper atom. The remaining atoms were located by Fourier-difference maps. Refinement was by full-matrix least squares on F^2. Hydrogen atoms were included in calculated positions except for those of the water molecule which were found by Fourier-difference map, and refined in riding mode with isotropic thermal vibrational parameters related to those of the supporting atoms. Refinement converged at a final R (observed data) = 0.0466 (wR_2 = 0.1227 for all 3844 unique reflections, 307 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.46 and 0.57 e $Å^{-3}$. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0662\ P)^2 + 2.66\ P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL 93[16] as implemented on a Viglen 486dx computer.

Complex **15**. A crystal having dimensions of 0.75 × 0.60 × 0.10 mm was used to collect X-ray data at room temperature in the range $3.5 < 2\theta < 45.0°$ on a Siemens P4 diffractometer by the ω-scan method ($-1 \leqslant h \leqslant 15, -1 \leqslant k \leqslant 8, -27 \leqslant l \leqslant 26$). The 4971 measured reflections yielded 3597 unique and 2752 independent reflections with $|F|/\sigma(|F|) > 4.0$; all data were corrected for Lorentz and polarization effects and for absorption based upon semiempirical Ψ scans (maximum and minimum transmission coefficients 0.991 and 0.670). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode with isotropic thermal vibrational parameters related to those of the supporting atoms. Refinement converged at a final R (observed data) = 0.0702 (wR_2 = 0.2081 for all 3597 unique data, 343 parameters, mean and maximum δ/σ 0.009, 0.165), with allowance for the thermal anisotropy of all non-hydrogen atoms; the solvent molecule atoms were restrained to have common anisotropic components within 0.025 standard deviations. Minimum and maximum final electron density −1.07 and 0.79 e $Å^{-3}$. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1500\ P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. The source of complex scattering factors was as for complex **14**.

Table 1 Elemental analyses for the complexes with calculated values in parentheses

	Analysis (%)		
Compound	C	H	N
1 $[(CuL^1)_2][ClO_4]_2\cdot H_2O$	48.9 (49.0)	4.4 (4.3)	8.8 (8.6)
2 $[CuL^1(O_2CCMe_3)]\cdot H_2O$	59.8 (59.9)	6.4 (6.2)	8.2 (8.4)
3 $[(CuL^2)_2[ClO_4]_2\cdot H_2O$	49.9 (50.0)	4.4 (4.6)	8.2 (8.3)
4 $[(CuL^2)_2][CF_3SO_3]_2$	48.7 (48.8)	4.1 (4.1)	7.5 (7.7)
7 $[(CuL^3)_2][ClO_4]_2\cdot 2H_2O$	44.2 (44.1)	4.1 (3.9)	10.1 (10.3)
8 $[(CuL^3)_2][BF_4]_2\cdot 2H_2O$	45.4 (45.2)	3.8 (4.0)	10.6 (10.5)
9 $[CuL^3(Cl)]\cdot H_2O$	49.9 (50.0)	4.3 (4.4)	11.6 (11.7)
10 $[CuL^3(O_2CCMe_3)]\cdot H_2O$	54.5 (55.0)	5.6 (5.5)	10.1 (10.3)
11 $[(CuL^4)_2][ClO_4]_2\cdot 2H_2O$	45.4 (45.2)	4.2 (4.1)	9.9 (10.0)
12 $[(CuL^4)_2][BF_4]_2\cdot 2H_2O$	46.5 (46.2)	4.1 (4.2)	10.4 (10.3)
13 $[CuL^4(Cl)]\cdot 2H_2O$	49.0 (49.2)	4.9 (4.9)	10.5 (10.9)
14 $[CuL^4(O_2CMe)]\cdot H_2O$	52.9 (53.3)	5.1 (5.1)	10.7 (10.8)
15 $[CuL^4(SCN)]\cdot MeCO_2Et$	52.9 (53.2)	4.8 (5.0)	12.1 (11.9)

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

Results and Discussion

Cognisant that the copper(II) atom at the active centre of GOase is present in a five-co-ordinated square-pyramidal environment, phenol-bearing tripodal ligands that result in the formation of five-co-ordinate complexes of copper(II) with the donor atoms of the ligands occupying four of the five co-ordination sites were employed in this study. Tripodal ligands capable of forming five-membered chelate rings have been shown to impose a trigonal-bipyramidal geometry at copper(II) with a fifth ligand occupying the apical position *trans* to the tertiary amino nitrogen atom of the tripod.[17–20] Sterically more flexible tripodal ligands that can form one or more six-membered chelate rings favour the generation of a square-pyramidal geometry where the fifth ligand occupies a basal position of the pyramid.[6,19,21–24] Consequently a series of tripodal ligands capable of forming two or three six-membered chelate rings at the metal and bearing a phenolic moiety, to resemble the amino acid tyrosine, were employed in our investigations.

In the presence of the weak base triethylamine, the phenolic group in the pro-ligand (HL) is readily deprotonated to form five-co-ordinate copper(II) complexes. If copper(II) salts derived from weakly co-ordinating anions such as perchlorate, tetrafluoroborate or trifluoromethanesulfonate were used in the syntheses the complexes formed tended to be dimers in which two copper(II) atoms share the phenolate oxygens from two

Table 2 Positive-ion FAB mass spectral assignments for complexes

Compound	Anion (X^-)	m/z $[Cu_2L_2(X)]^+$	 $[Cu_2L_2 - H]^+$	 $[LCu_2O - H]^+$	 $[Cu_2L - 2H]^+$	 $[CuL]^+$
(*a*) L = L^1						
1[a]	ClO_4^-	862	763	459	446	382
2[b]	$Me_3CCO_2^-$	866	763			381
(*b*) L = L^2						
3[a]	ClO_4^-	876		475	460	395
4[c]	$CF_3SO_3^-$	939			460	395
5[b]	Cl^-	827				395
6[b]	N_3^-	834				395
(*c*) L = L^3						
7[b]	ClO_4^-	953	855		491	427
8[b]	BF_4^-	939	855	506	491	427
9[b]	Cl^-	890	855			427
10[b]	$Me_3CCO_2^-$					426
(*d*) L = L^4						
11[b]	ClO_4^-	980	881	520	505	440
12[a]	BF_4^-	954	882		505	441
13[c]	Cl^-					440
14[b]	$MeCO_2^-$					440
15[b]	SCN^-	940				440

Where no value is given no peak was apparent over the background noise. [a] Glycerol matrix. [b] 3-Nitrobenzyl alcohol matrix. [c] 3-Nitrobenzyl alcohol–trifluoroacetic acid matrix.

ligands. Addition of *p*-cresol, phenol or imidazole to the above reactions followed by adjustment to pH ≈ 9.0 using 3 mol dm^{-3} NaOH to induce deprotonation of these ligands still gave only the dimeric products. Mononuclear copper(II) complexes can be obtained in the presence of more strongly co-ordinating anions such as $MeCO_2^-$, Cl^-, $Me_3CCO_2^-$, N_3^- and SCN^-; even simple addition of the sodium salts of the latter pair of anions to a solution containing the appropriate dimer leads to a monomeric product. When acetate was introduced into the co-ordination sphere of copper(II) it was found to occupy a basal site of the square-pyramidal environment (Fig. 1) so deriving a structural analogue for the basal plane of the copper(II) site in GOase.

Table 3 Carboxylate modes ν_{asym} and ν_{sym} in the IR spectra[a] for complexes **2**, **10** and **14**

Complex	R in RCO_2^-	ν_{asym}	ν_{sym}
2	Me_3C	1562[b]	1400
10	Me_3C	1568[b]	1396
14	Me	1562[b]	1387

[a] In cm^{-1} (KBr disc). [b] Partly overlapping with ligand bands.

Spectroscopic Characterization.—The principal peaks in the positive-ion fast-atom bombardment (FAB) mass spectra of the complexes are reported in Table 2. The solvent molecules in the complexes are readily lost and not observed. For compounds **3**, **14** and **15** for which crystal structures have been solved the following pattern emerged. For the dinuclear complex **3** a molecular ion peak was found at *m/z* 876, $[Cu_2L^2_2(ClO_4)]^+$, together with a mononuclear fragment at *m/z* 395, $[CuL^2]^+$, and two other dinuclear peaks at *m/z* 475 and 460 assigned to $[L^2Cu_2O - H]^+$ and $[L^2Cu_2 - 2H]^+$ respectively. The mononuclear complex **14** showed a parent peak at *m/z* 440 assigned to $[CuL^4]^+$ and with no evidence for dinuclear fragments. Complex **15** which was shown to have a monomeric structure gave peaks corresponding to both di- {*m/z* = 940, $[Cu_2L^4_2(SCN)]^+$} and mono-nuclear species (*m/z* = 440 $[CuL^4]^+$). Compounds **10** and **13** follow the same pattern as for **14** but all of the other complexes give evidence of peaks, often weak, attributable to dinuclear complexes. It is therefore difficult to assign structures with total certainty on the basis of the FAB mass spectrum. This propensity for higher aggregation in complexes in which there is a pathway for dimerization has been noted previously.[25]

In the IR spectra (KBr disc) of the dimeric complexes distinct absorptions corresponding to the unco-ordinated anions are observed as strong bands at 1083 cm^{-1} for BF_4^-, 1093 and 623 cm^{-1} for ClO_4^-, and 1257, 1150, 1030 and 637 cm^{-1} for $CF_3SO_3^-$. For complexes in which the carboxylate is co-ordinated the antisymmetric and symmetric stretching modes of the carboxylate occur *ca.* 1560 and 1400 cm^{-1} (see Table 3),[26] the antisymmetric bands are partly overlapped by ligand bands. For complex **15** the strong band observed at 2093 cm^{-1} is assigned to co-ordinated SCN^- and the medium-intensity absorption at 1736 cm^{-1} is assigned to the ethyl acetate in the molecule. A band at 2041 cm^{-1} for compound **6** is attributed to co-ordinated azide.[15]

The electronic spectral data for the present complexes are summarized in Table 4. The intense absorbance bands occurring in the range 370–460 nm are assigned, by comparison with the spectral features of complexes of related ligands,[7,15] to equatorial $O^- \rightarrow Cu^{II}$ charge-transfer transitions. For the complexes derived from HL^3 and HL^4 this charge-transfer transition shifts to higher energy (450 to 400 nm) and intensifies significantly; this is accounted for by the presence of the strongly electron-withdrawing NO_2 group. The band at 405 nm (ε = 2310 dm^3 mol^{-1} cm^{-1}) of complex **6** is ascribed to a $N_3^- \rightarrow Cu^{II}$ charge-transfer transition.[15] The position of the ligand-field bands suggests that in solution the Cu^{II} atoms in the complexes, with the exception of **1** and **13**, have similar square-pyramidal geometries.[7,15] Complexes **1** and **13** display lower-energy bands suggesting that changes have occurred in the geometry around copper(II) and indicating the presence of a more trigonal-bipyramidal element in solution.[27]

Table 4 Electronic spectra (λ/nm, ε/dm^3 mol^{-1} cm^{-1} in parentheses) for the complexes in MeCN

Compound	Ligand based[a]	Charge transfer[a]		Ligand field[b]
1[c]	257 (12 600) 287 (6 400)[d]		438 (600)	780 (140)
2[c]	253 (12 900) 300 (4 300)[d]		460 (400)	670 (110)
3[c]	263 (13 000)		439 (4 000)	660 (365)
4[c]	262 (10 200)		439 (3 150)	660 (350)
5[e]	260 (11 200)		440 (1 940)	670 (220)
6[e]	240 (11 400)	405 (2 310)	465 (1 380)	650 (260)
7[c]	257 (13 200)	401 (25 800)		655 (175)
8[c]	256 (15 500)	400 (28 200)		640 (165)
9	257 (17 100)	400 (30 000)		680 (210)
10	257 (12 000)	404 (23 500)		645 (140)
11[c]	260 (14 600)	374 (21 600)	495 (1 480)	675 (190)
12[c]	258 (13 200)	374 (19 000)		680 (150)
13	257 (7 800)	378 (15 300)		760 (160)[f]
14	260 (11 000)	395 (19 000)		675 (320)
15	259.2 (12 082)	385.8 (18 885)		665 (225)

[a] ≈ 1.0×10^{-4} mol dm^{-3}. [b] ≈ 1.5×10^{-3} mol dm^{-3}. [c] Concentrations were calculated based on the monomer. [d] Shoulder. [e] Data taken from ref. 15. [f] $HCONMe_2$–MeCN (1 : 1) medium.

Table 5 Selected bond lengths (Å) and angles (°) for complex **14** with estimated standard deviations (e.s.d.s)

Cu–O(4)	1.970(2)	N(2)–C(11)	1.443(5)	C(2)–C(3)	1.376(8)	C(12)–C(13)	1.388(5)
Cu–O(1)	1.982(3)	N(3)–C(7)	1.493(4)	C(3)–C(4)	1.370(7)	C(13)–C(14)	1.494(5)
Cu–N(4)	2.046(3)	N(3)–C(15)	1.494(4)	C(4)–C(5)	1.390(6)	C(15)–C(16)	1.519(5)
Cu–N(3)	2.085(3)	N(3)–C(14)	1.507(4)	C(5)–C(6)	1.506(6)	C(16)–C(17)	1.499(5)
Cu–N(1)	2.265(3)	N(4)–C(17)	1.341(5)	C(6)–C(7)	1.531(5)	C(17)–C(18)	1.380(5)
Cu • • • O(5)	2.713(2)	N(4)–C(21)	1.358(5)	C(8)–C(9)	1.412(5)	C(18)–C(19)	1.390(7)
N(1)–C(1)	1.338(5)	O(1)–C(8)	1.305(4)	C(8)–C(13)	1.424(5)	C(19)–C(20)	1.367(7)
N(1)–C(5)	1.340(5)	O(4)–C(22)	1.285(5)	C(9)–C(10)	1.380(5)	C(20)–C(21)	1.377(6)
N(2)–O(3)	1.227(4)	O(5)–C(22)	1.233(5)	C(10)–C(11)	1.397(5)	C(22)–C(23)	1.517(5)
N(2)–O(2)	1.230(4)	C(1)–C(2)	1.372(7)	C(11)–C(12)	1.390(5)		

O(4)–Cu–O(1)	85.53(10)	C(7)–N(3)–C(15)	109.5(3)	N(1)–C(5)–C(4)	121.7(4)	C(12)–C(13)–C(14)	119.1(3)
O(4)–Cu–N(4)	88.12(11)	C(7)–N(3)–C(14)	109.0(3)	N(1)–C(5)–C(6)	116.7(3)	C(8)–C(13)–C(14)	121.0(3)
O(1)–Cu–N(4)	171.92(11)	C(15)–N(3)–C(14)	105.8(3)	C(4)–C(5)–C(6)	121.5(4)	C(13)–C(14)–N(3)	116.0(3)
O(4)–Cu–N(3)	167.38(11)	C(7)–N(3)–Cu	111.5(2)	C(5)–C(6)–C(7)	113.3(3)	N(3)–C(15)–C(16)	114.0(3)
O(1)–Cu–N(3)	93.16(10)	C(15)–N(3)–Cu	113.8(2)	N(3)–C(7)–C(6)	113.7(3)	C(17)–C(16)–C(15)	110.4(3)
N(4)–Cu–N(3)	91.95(12)	C(14)–N(3)–Cu	107.1(2)	O(1)–C(8)–C(9)	120.6(3)	N(4)–C(17)–C(18)	121.9(4)
O(4)–Cu–N(1)	98.76(12)	C(17)–N(4)–C(21)	119.0(3)	O(1)–C(8)–C(13)	121.0(3)	N(4)–C(17)–C(16)	115.7(3)
O(1)–Cu–N(1)	90.31(12)	C(17)–N(4)–Cu	121.4(2)	C(9)–C(8)–C(13)	118.4(3)	C(18)–C(17)–C(16)	122.2(4)
N(4)–Cu–N(1)	95.60(13)	C(21)–N(4)–Cu	119.4(3)	C(10)–C(9)–C(8)	121.8(4)	C(17)–C(18)–C(19)	118.8(4)
N(3)–Cu–N(1)	93.79(12)	C(8)–O(1)–Cu	129.6(2)	C(9)–C(10)–C(11)	118.5(4)	C(20)–C(19)–C(18)	119.2(4)
C(1)–N(1)–C(5)	118.2(4)	C(22)–O(4)–Cu	107.3(2)	C(12)–C(11)–C(10)	121.4(3)	C(19)–C(20)–C(21)	119.8(4)
C(1)–N(1)–Cu	119.2(3)	N(1)–C(1)–C(2)	123.2(5)	C(12)–C(11)–N(2)	118.8(3)	N(4)–C(21)–C(20)	121.2(4)
C(5)–N(1)–Cu	122.5(3)	C(1)–C(2)–C(3)	118.3(5)	C(10)–C(11)–N(2)	119.8(3)	O(5)–C(22)–O(4)	123.5(4)
O(3)–N(2)–O(2)	122.1(3)	C(4)–C(3)–C(2)	119.5(5)	C(13)–C(12)–C(11)	120.2(3)	O(5)–C(22)–C(23)	120.7(4)
O(3)–N(2)–C(11)	119.0(3)	C(3)–C(4)–C(5)	119.0(5)	C(12)–C(13)–C(8)	119.6(3)	O(4)–C(22)–C(23)	115.8(4)
O(2)–N(2)–C(11)	118.9(3)						

Structures of the Complexes.—The crystal structure of complex **3** has been reported previously.[9] The complex is a dimer in the solid state; the molecular dication is centrosymmetric and comprises two related copper(II) ions which are asymmetrically bridged by a pair of phenolic oxygen atoms from the two symmetry-equivalent tetradentate ligands.

The molecular structures of complexes **14** and **15** are depicted in Figs. 1 and 2 respectively. The atomic positional parameters are given, together with their standard deviations, in Tables 9 and 10. Selected bond lengths and bond angles, with standard deviations in parentheses, are presented in Tables 5 and 6.

In the crystal structure of complex **14** the asymmetric unit comprises one mononuclear copper(II) complex molecule and one water molecule. The copper atom is bonded to the four heteroatoms provided by the anionic ligand L^4 and to the acetate anion in an approximately square-pyramidal co-ordination environment, in which atoms O(1), N(3), N(4) and O(4) make up the basal plane [root mean square (r.m.s.) deviation 0.061 Å; with O(1) −0.062, N(3) 0.056, N(4) −0.060, O(4) 0.066, N(1) −2.422 Å out of planarity] with a very small $\tau = 0.076$.[28] The copper(II) ion lies 0.161 Å above this basal plane in the direction of N(1) and axially co-ordinates to this pyridine nitrogen [Cu–N(1) 2.265 Å]. The acetate group is primarily monodentate, Cu–O 1.970 Å, but the second oxygen is directed back towards the metal with a long Cu • • • O interaction of 2.713 Å.

The pyridinyl and phenolate rings are planar (r.m.s. deviations 0.008, 0.008 and 0.012 Å respectively), with angles between six-membered ring planes of 78.4, 91.9 and 31.0°. The nitro group is asymmetrically twisted by 7.0° with respect to the phenyl ring. Torsion angles of (amine) N–C–C–C (pyridine) are −88.3 and −78.7° respectively. The co-ordinated phenolate

Table 6 Selected bond lengths (Å) and angles (°) for complex **15**

Cu–O(1)	1.938(4)	N(2)–C(10)	1.354(7)	C(1)–C(6)	1.411(9)	C(11)–C(12)	1.372(10)
Cu–N(4)	2.012(6)	N(3)–C(21)	1.338(8)	C(2)–C(3)	1.372(10)	C(12)–C(13)	1.375(11)
Cu–N(2)	2.026(5)	N(3)–C(17)	1.345(8)	C(3)–C(4)	1.364(10)	C(13)–C(14)	1.350(9)
Cu–N(1)	2.100(4)	N(4)–C(22)	1.139(8)	C(4)–C(5)	1.382(9)	C(15)–C(16)	1.533(8)
Cu–N(3)	2.205(5)	N(5)–O(2)	1.213(8)	C(5)–C(6)	1.388(8)	C(16)–C(17)	1.491(9)
S–C(22)	1.603(7)	N(5)–O(3)	1.256(8)	C(6)–C(7)	1.499(8)	C(17)–C(18)	1.397(9)
N(1)–C(7)	1.502(7)	N(5)–C(4)	1.458(8)	C(8)–C(9)	1.518(9)	C(18)–C(19)	1.359(11)
N(1)–C(15)	1.504(7)	O(1)–C(1)	1.311(7)	C(9)–C(10)	1.498(9)	C(19)–C(20)	1.397(11)
N(1)–C(8)	1.505(7)	C(1)–C(2)	1.396(9)	C(10)–C(11)	1.351(9)	C(20)–C(21)	1.379(10)
N(2)–C(14)	1.351(8)						
O(1)–Cu–N(4)	85.9(2)	C(8)–N(1)–Cu	111.7(3)	C(3)–C(2)–C(1)	121.1(7)	C(10)–C(11)–C(12)	121.1(6)
O(1)–Cu–N(2)	161.1(2)	C(14)–N(2)–C(10)	118.1(5)	C(4)–C(3)–C(2)	119.1(7)	C(13)–C(12)–C(11)	117.9(6)
N(4)–Cu–N(2)	85.5(2)	C(14)–N(2)–Cu	121.0(4)	C(3)–C(4)–C(5)	122.0(6)	C(14)–C(13)–C(12)	119.4(7)
O(1)–Cu–N(1)	93.6(2)	C(10)–N(2)–Cu	119.5(4)	C(3)–C(4)–N(5)	118.1(6)	C(13)–C(14)–N(2)	122.6(7)
N(4)–Cu–N(1)	167.9(2)	C(21)–N(3)–C(17)	119.9(6)	C(5)–C(4)–N(5)	119.9(6)	N(1)–C(15)–C(16)	114.3(5)
N(2)–Cu–N(1)	91.3(2)	C(21)–N(3)–Cu	118.3(4)	C(4)–C(5)–C(6)	119.6(6)	C(17)–C(16)–C(15)	112.0(5)
O(1)–Cu–N(3)	98.0(2)	C(17)–N(3)–Cu	121.8(4)	C(5)–C(6)–C(1)	119.2(6)	N(3)–C(17)–C(18)	120.5(6)
N(4)–Cu–N(3)	97.5(2)	C(22)–N(4)–Cu	168.2(5)	C(5)–C(6)–C(7)	121.3(6)	N(3)–C(17)–C(16)	117.4(5)
N(2)–Cu–N(3)	99.8(2)	O(2)–N(5)–O(3)	121.7(6)	C(1)–C(6)–C(7)	119.5(5)	C(18)–C(17)–C(16)	122.2(6)
N(1)–Cu–N(3)	94.5(2)	O(2)–N(5)–C(4)	121.5(7)	C(6)–C(7)–N(1)	113.0(5)	C(19)–C(18)–C(17)	120.0(7)
C(7)–N(1)–C(15)	108.0(4)	O(3)–N(5)–C(4)	116.7(6)	N(1)–C(8)–C(9)	114.0(5)	C(18)–C(19)–C(20)	119.0(7)
C(7)–N(1)–C(8)	106.9(4)	C(1)–O(1)–Cu	123.6(4)	C(10)–C(9)–C(8)	110.8(5)	C(21)–C(20)–C(19)	118.9(7)
C(15)–N(1)–C(8)	108.9(4)	O(1)–C(1)–C(2)	120.2(6)	C(11)–C(10)–N(2)	120.8(6)	N(3)–C(21)–C(20)	121.7(7)
C(7)–N(1)–Cu	109.4(3)	O(1)–C(1)–C(6)	120.8(6)	C(11)–C(10)–C(9)	123.6(6)	N(4)–C(22)–S	178.5(6)
C(15)–N(1)–Cu	111.9(3)	C(2)–C(1)–C(6)	119.0(6)	N(2)–C(10)–C(9)	115.4(5)		

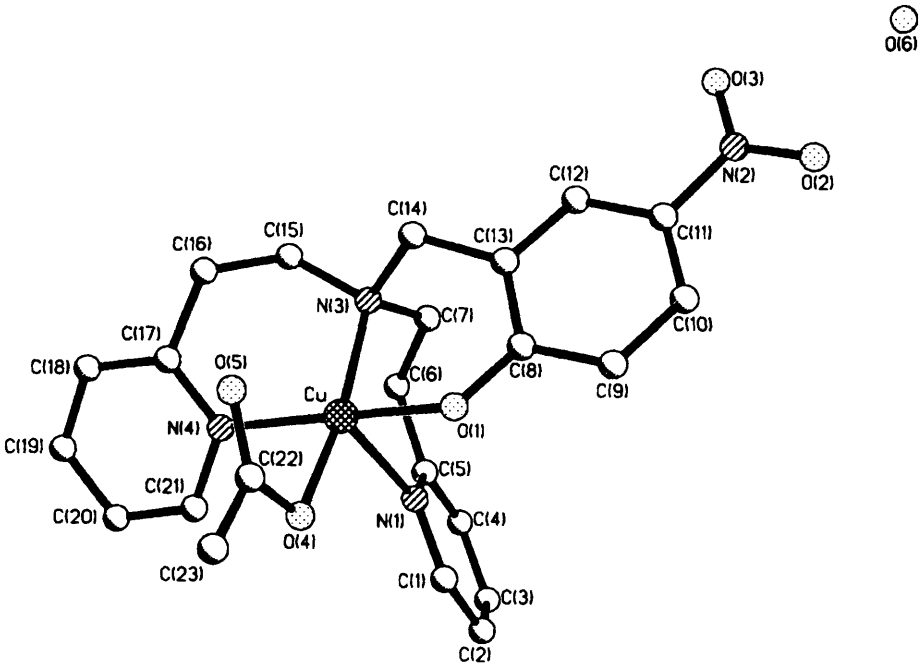

Fig. 1 Molecular structure of complex **14**, [CuL^4(O$_2$CMe)]·H$_2$O

oxygen is hydrogen bonded to a solvent water molecule [O(1)···O(6) 2.870, O(1)···H(6B) 1.90 Å], which also links to a symmetry-related nitro group oxygen [O(6)···O(3) ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$) 3.175 Å, H(6A)···O(3) 2.33 Å] through a longer, but angularly appropriate interaction.

The asymmetric unit of structure **15** comprises a mononuclear copper(II) complex and one ethyl acetate solvent molecule. The copper atom is bound in a five-co-ordinated distorted square-pyramidal environment provided by four donor atoms of ligand L^4 and a NCS group, r.m.s. deviation of basal plane 0.044 Å, deviation of Cu(1) −0.259 Å towards axial N(3). The copper–donor atom distances within the square base co-ordination plane range between 1.938 and 2.100 Å, and the largest is for the axial position, 2.205 Å. The SCN$^-$ ligand is nearly linear with N(4)–C(22)–S 178.5° and co-ordinates to the copper(II) through the nitrogen atom, C(22)–N(4)–Cu 168.2°.

The phenyl and pyridinyl rings are planar (r.m.s. deviations 0.007, 0.008 and 0.005 Å), and the deviations from planarity of the oxygen and nitrogen substituent atoms of the phenyl ring are small (−0.032 and −0.028 Å). The nitro group is asymmetrically twisted by 5.6° from the plane of the phenyl ring. The angles between the pyridinyl and phenyl groups are 87.9, 44.5 and 112.1° respectively. Torsion angles within (pyridinyl) C–C–C–N (amine) chelate groups are −80.1 and −86.6°.

Structural Comparison and Biological Relationship.—A comparison of the structural parameters for complexes **3**, **14**

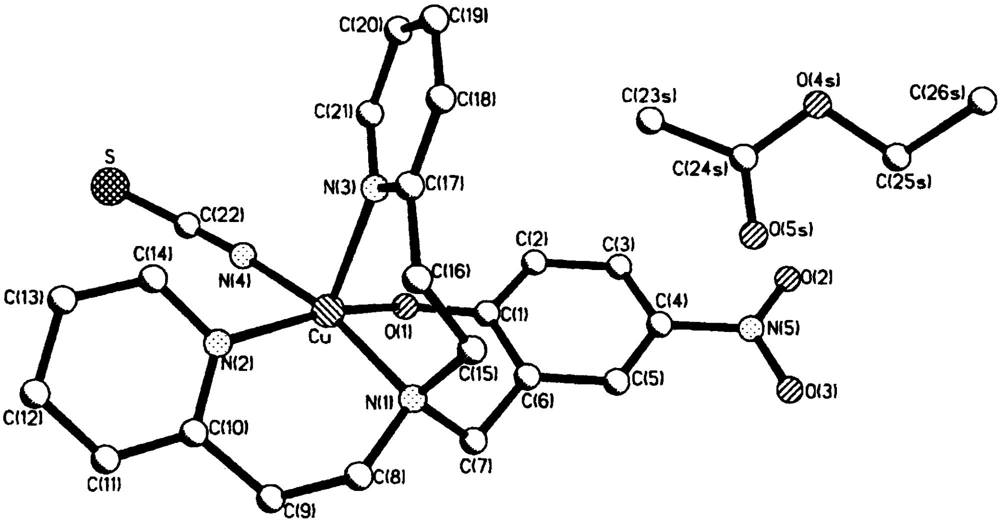

Fig. 2 Molecular structure of complex **15**, [CuL^4(SCN)]·MeCO$_2$Et

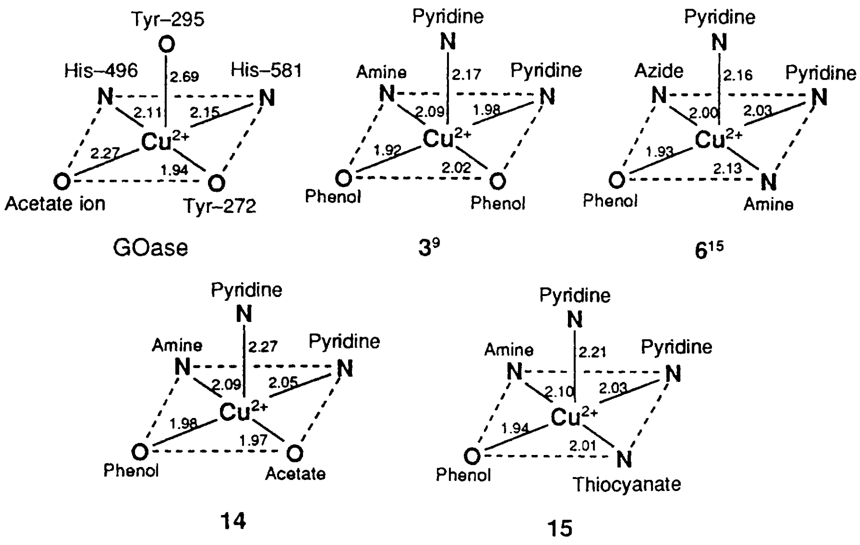

Fig. 3 Comparison of copper(II) co-ordination environments

Table 7 Comparison of some structural parameters for copper(II) co-ordination spheres

Compound	τ*	r.m.s. deviation of basal plane/Å	Deviation of Cu above plane/Å	Axial bond length Cu–N$_{py}$/Å
3^9	0.17	0.093	0.271	2.168
6^{15}	0		0.23	2.162
14	0.08	0.061	0.161	2.265
15	0.11	0.044	0.259	2.205

* For perfect tetragonal and trigonal-bipyramidal geometries the values of τ are zero and unity respectively; τ being an index of the degree of trigonality within the structural continuum between square-planar and trigonal-bipyramidal geometries.[28]

and **15** reveals that, except for minor differences, the three compounds are closely similar with respect to the co-ordination geometry about the copper(II) atom (Fig. 3). Table 7 lists some structural parameters of these complexes together with those for **6**.[15] In the present three complexes the geometries around copper(II) are best described as distorted square pyramidal with a small trigonal-bipyramidal component from τ = 0.08 to 0.17. The present structures are very similar to that of the azide complex **6** but differ from that of the related copper(II) chloride complex [CuL^5(Cl)],[7] in which two pyridyl nitrogens co-ordinate equatorially to copper(II) and the phenolate occupies the apical position. It was proposed that the apical co-ordination of the phenolate was due to the introduction of the electron-withdrawing NO$_2$ group *para* to the phenolic group as in its absence phenolates had been found only to occupy equatorial positions. This may be related to the polarity rule, noted for main-group chemistry, which states that the more electronegative ligand will preferentially occupy the axial position of a tetragonal based pyramid.[29] This proposal is at odds with the structural information given here where equatorially sited *p*-nitrophenolates are observed. We note however that in [CuL^5(Cl)] a 5,5,6-membered chelate ring sequence is observed at the copper(II) atom whereas in **3**, **14** and **15** 6,6,6-membered chelate ring sequences are found and so it is suggested that steric factors are also involved and that the nature of the chelate rings formed may be more important than has previously been recognized.

In complex **14** there is a discrete mononuclear square-

Table 8 Experimental details of the crystal structure determinations*

Complex	**14**	**15**
Formula	$C_{23}H_{26}CuN_4O_6$	$C_{26}H_{29}CuN_5O_5S$
M	518.02	587.14
a/Å	9.734(4)	14.815(7)
b/Å	10.095(2)	7.646(2)
c/Å	24.525(12)	25.462(7)
β/°	100.84(3)	105.95(3)
U/Å^3	2367(2)	2773(2)
D_c/g cm^{-3}	1.454	1.406
F(000)	1076	1220
μ(Mo-Kα)/cm^{-1}	9.7	9.1
Total no.of unique data	3844	3597
Observed data [$\|F\|/\sigma(\|F\|) > 4.0$]	3240	2752
R	0.0466	0.0702
wR_2	0.1227	0.2081
Goodness of fit	1.038	1.065
Largest peak/e Å^{-3}	0.567	0.788

* Details in common: blue; monoclinic, space group $P2_1/n$; $Z = 4$.

Table 9 Final fractional atomic coordinates (× 10^4) for complex **14**

Atom	x	y	z	Atom	x	y	z
Cu	1800(1)	611(1)	1306(1)	C(7)	3247(4)	3040(3)	1807(2)
N(1)	2735(4)	1859(3)	700(1)	C(8)	4671(4)	−168(3)	1880(1)
N(2)	8207(3)	399(3)	3156(1)	C(9)	5972(4)	−749(4)	1847(2)
N(3)	2370(3)	1939(3)	1961(1)	C(10)	7131(4)	−591(4)	2263(2)
N(4)	−164(3)	1405(3)	1106(1)	C(11)	7019(4)	227(4)	2712(2)
O(1)	3569(3)	−403(2)	1499(1)	C(12)	5769(4)	854(4)	2750(2)
O(2)	9275(3)	−248(4)	3149(1)	C(13)	4584(3)	646(3)	2346(1)
O(3)	8126(3)	1195(3)	3527(1)	C(14)	3210(4)	1173(4)	2437(1)
O(4)	1130(3)	−888(2)	813(1)	C(15)	1155(4)	2502(4)	2176(2)
O(5)	448(4)	−1537(3)	1584(1)	C(16)	−127(4)	1613(4)	2086(2)
O(6)	3732(3)	−2961(3)	1004(2)	C(17)	−901(4)	1715(4)	1498(2)
C(1)	3066(5)	1284(5)	251(2)	C(18)	−2258(4)	2176(5)	1367(2)
C(2)	3564(6)	1975(6)	−153(2)	C(19)	−2860(5)	2358(5)	812(2)
C(3)	3689(5)	3329(6)	−101(2)	C(20)	−2113(5)	2030(5)	412(2)
C(4)	3365(5)	3939(5)	357(2)	C(21)	−772(5)	1547(4)	563(2)
C(5)	2898(4)	3173(4)	757(2)	C(22)	572(4)	−1729(4)	1099(2)
C(6)	2573(4)	3779(4)	1279(2)	C(23)	92(5)	−3021(4)	809(2)

Table 10 Final fractional atomic coordinates (× 10^4) for complex **15**

Atom	x	y	z	Atom	x	y	z
Cu	4855(1)	2035(1)	1668(1)	C(10)	6638(4)	1184(8)	2476(2)
S	6431(2)	5967(3)	790(1)	C(11)	7577(4)	957(9)	2656(3)
N(1)	4433(3)	411(6)	2222(2)	C(12)	8109(5)	724(9)	2298(3)
N(2)	6193(3)	1150(7)	1935(2)	C(13)	7652(5)	649(10)	1750(3)
N(3)	4319(4)	280(7)	965(2)	C(14)	6713(5)	871(9)	1583(3)
N(4)	5386(4)	3890(7)	1278(2)	C(15)	3980(4)	−1244(8)	1956(2)
N(5)	269(4)	1235(9)	1630(3)	C(16)	4515(5)	−2153(7)	1596(3)
O(1)	3766(3)	3540(6)	1553(2)	C(17)	4246(4)	−1456(8)	1028(2)
O(2)	−427(4)	1605(9)	1268(3)	C(18)	3919(5)	−2539(10)	573(3)
O(3)	220(3)	373(8)	2041(3)	C(19)	3657(6)	−1837(11)	63(3)
C(1)	2942(4)	2998(8)	1584(3)	C(20)	3721(6)	−28(11)	4(3)
C(2)	2127(5)	3534(10)	1195(3)	C(21)	4065(5)	982(10)	464(3)
C(3)	1261(5)	2941(10)	1211(3)	C(22)	5812(4)	4747(9)	1069(2)
C(4)	1197(4)	1851(8)	1623(3)	O(4s)	−140(7)	−2527(20)	358(4)
C(5)	1981(4)	1319(8)	2026(3)	O(5s)	877(11)	−2351(19)	1182(4)
C(6)	2864(4)	1881(8)	2010(2)	C(23s)	1428(7)	−1206(23)	471(7)
C(7)	3730(4)	1364(8)	2444(2)	C(24s)	696(7)	−2020(21)	700(4)
C(8)	5244(4)	−59(8)	2704(2)	C(25s)	−757(10)	−2989(23)	665(6)
C(9)	6011(4)	1317(9)	2846(2)	C(26s)	−1319(12)	−4622(22)	413(8)

pyramidal geometry with an equatorial acetate–copper(II) bond. This structure, with an acetate oxygen *trans* to an amine nitrogen and a phenolate oxygen *trans* to pyridinyl nitrogen, may be compared with the ligand disposition in GOase where there is an acetate oxygen *trans* to a histidine nitrogen and a tyrosine oxygen *trans* to another histidine oxygen in GOase (Fig. 3). We are currently attempting to introduce an apical phenolate into such a system in order to move closer to a structural model for the natural system.

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