# Formation of axial phenolate–metal bonds in square-pyramidal complexes†

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Copper(II) complexes derived from tripodal ligands capable of forming 5,6,6- or 5,5,6-membered chelate ring sequences have been synthesised and characterised. The crystal structures of two complexes [CuL($O_2CBu^t$)]·MeCN [HL = (2-hydroxy-5-nitrophenylmethyl)(pyridin-2-ylethyl)(pyridin-2-ylmethyl)amine] and [CuL($O_2CMe$)]·$H_2O$ [HL = (2-hydroxy-5-nitrophenylmethyl)bis(pyridin-2-ylmethyl)amine] have been solved. They are neutral, mononuclear copper(II) species in the solid state. In contrast to copper(II) complexes derived from related tripodal ligands forming 6,6,6-membered chelate rings, the present complexes have an axial phenolate–copper(II) bond in their square-pyramidal structures. The formation of this bond is related to the steric factors arising from the flexibility of the ligand pendant arms. The complex [CuL($O_2CMe$)] exhibits structural features related to the biosite in galactose oxidase; an acetate co-ordinates to copper equatorially and a phenolate oxygen atom occupies the axial position.

Following a report of the crystal structure of galactose oxidase (GOase) we have carried out a programme of research aimed at synthesising small molecule complexes as models for the copper biosite present in this enzyme. The structure of the active site in GOase crystallised from an acetate buffer (pH 4.5) has been shown to have quite distinct co-ordination features.[2] The geometry around the monomeric copper(II) centre can be described as square pyramidal; the copper(II) ion is co-ordinated to four amino acid residues from the protein chain and one exogenous acetate anion. The almost perfect square comprises one tyrosine oxygen atom, two histidine nitrogen atoms and an acetate oxygen atom; a further tyrosine oxygen atom occupies the apical position of the pyramid (Fig. 1).

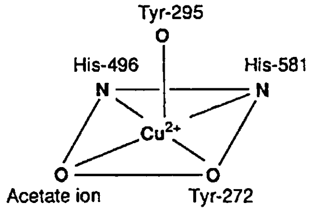
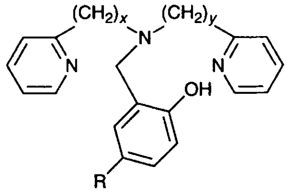


**Fig. 1** The copper(II) site in galactose oxidase

We have previously reported a series of copper(II) complexes derived from ligands bearing pyridyl and phenolic groups,[1,3] in which one key feature is that a pyridine nitrogen atom occupies the axial position in the observed square-pyramidal co-ordination geometry. In order to obtain a closer synthetic model for the biosite in GOase effort has been made to prepare complexes with an axial phenolate oxygen–copper(II) bond in order to simulate the tyrosine oxygen–copper(II) axial bond found at the active site of the enzyme. A mononuclear copper(II) complex [CuL$^6$(Cl)], derived from proligand HL$^6$, has been reported to have such an unusual axial oxygen–copper(II) bond[4] and the authors proposed that the main contribution to the formation of such a bond was from the introduction of the electron-withdrawing $NO_2$ group *para* to the phenolic group as in the absence of this substituent phenolates had been found only to occupy equatorial positions as in the complex [CuL$^1$($N_3$)].[5] This proposal is at odds with the structural information given in our earlier paper in which complexes with equatorially sited *p*-nitrophenolates are observed.[1] It was noted that in [CuL$^6$(Cl)] a 5,5,6-membered chelate ring sequence is present at the copper(II) atom whereas in complexes derived from proligands HL$^1$ and HL$^4$ 6,6,6-membered sequences are found and so it was suggested that steric factors are also involved in defining the axial ligation and that the nature of the chelate rings formed at the metal may be more important than has previously been recognised.[1] Therefore a series of copper(II) complexes derived from those proligands HL$^n$ ($n$ = 2, 3, 5 or 6) capable of forming 5,6,6- and 5,5,6-membered chelate ring sequences have been synthesised in order to investigate the effect of ligand steric factors on co-ordination of the metal. The results reported here reveal that an axial phenolate–copper(II) bond can be constructed by adjustment of the flexibility of the ligand pendant arms. A mononuclear copper(II) complex, [CuL$^6$($O_2CMe$)]·$H_2O$, which has an axial oxygen–copper bond and an equatorially bound acetate anion in its square-pyramidal structure, has been obtained.



| R = H | | R = $NO_2$ | |
|---|---|---|---|
| HL$^1$ | $x = y = 2$ | HL$^4$ | $x = y = 2$ |
| HL$^2$ | $x = 1, y = 2$ | HL$^5$ | $x = 1, y = 2$ |
| HL$^3$ | $x = y = 1$ | HL$^6$ | $x = y = 1$ |

## Experimental

### Materials and methods

Reagents and solvents used were of commercial reagent quality. Purification of the proligands was effected by using flash chromatography[6] with silica gel (40–63 μm). The identity and purity were judged by TLC, $^1H$ NMR and mass spectroscopy. All elemental analyses were carried out by the University of Sheffield Microanalytical Service. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 1600 Fourier-transform spectrophotometer (4000–400 cm$^{-1}$), electronic absorption spectra using a Philips PU8720 UV/VIS scanning spectrophotometer operating in the range 220–500 nm, $^1H$ NMR spectra at 220 MHz on a Perkin-Elmer R34 spectrometer and the $^{13}C$ NMR spectra (62.9 MHz) using a Bruker AM-250 spectrometer. Positive-ion fast atom bombardment (FAB) mass

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† Heteroleptic Tripodal Complexes of Copper(II). Part 2.[1]

spectra were recorded on a Kratos Ms 80 spectrometer using 3-nitrobenzyl alcohol as matrix unless otherwise stated.

### Proligand synthesis

The proligands were prepared according to literature procedures.[1] The analysis data for the new proligands are as follows.

$HL^3$: $^1H$ NMR ($CDCl_3$) δ 3.70 (s, 2 H, $CH_2$), 3.80 (s, 4 H, $2CH_2$), 6.65–7.55 (m, 10 H, aromatic), 8.55 (d, 2 H, $2C_5H_4N$) and 11.05 (s, 1 H, OH); $^{13}C$ NMR ($CDCl_3$) δ 56.9, 59.0, 116.5, 118.9, 122.2, 122.8, 123.2, 129.0, 130.2, 136.8, 148.8, 157.5 and 158.2; mass spectrum $m/z$ = 306 ($M^+$, 100), 213 (67) and 200 (36%).

$HL^6$: $^1H$ NMR ($CDCl_3$) δ 3.75 (s, 2 H, $CH_2$), 3.90 (s, 4 H, $2CH_2$), 6.90–8.05 (m, 9 H, aromatic) and 8.55 (d, 2 H, $2C_5H_4N$); $^{13}C$ NMR ($CDCl_3$) δ 56.1, 58.6, 117.2, 122.4, 123.0, 123.6, 125.6, 126.6, 137.1, 139.6, 148.6, 157.7, and 164.4; mass spectrum $m/z$ = 351 ($M^+$, 100), 258 (32) and 200 (45%).

### Complex synthesis

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

**$[CuL^5(O_2CBu^t)]\cdot MeCN$ 1.** This compound was previously reported as the monohydrate.[1] Recrystallisation of the monohydrate from acetonitrile–ethyl acetate (1:10) gave crystals suitable for X-ray analysis.

**$[CuL^5(O_2CMe)]$ 2.** The compound $Cu(O_2CMe)_2\cdot H_2O$ (1 mmol, 0.20 g) was dissolved in hot MeOH (40 $cm^3$) and the proligand (1 mmol, 0.34 g in 5 $cm^3$ MeOH) was added; the solution turned dark green. After addition of an equimolar amount of triethylamine, the mixture was heated to reflux for 1 h. On cooling the solvent was removed using a rotary evaporator. The residue was dissolved in MeOH (5 $cm^3$) and ethyl acetate (40 $cm^3$) was added while warming. A crystalline solid was obtained by leaving this mixed solution at room temperature for a few days (0.25 g, 52%).

**$[(CuL^3)_2][ClO_4]_2\cdot H_2O$ 3.** Equimolar amounts of proligand (1 mmol, 0.31 g) and $Cu(ClO_4)_2\cdot 6H_2O$ (0.37 g) were stirred in MeOH (50 $cm^3$), triethylamine (1 mmol, 0.11 g) was added and a green precipitate was formed immediately. The mixture was heated to reflux for 1 h. On cooling, the solid was filtered off and recrystallised from MeCN–MeOH (1:3) as dark green crystals (0.29 g, 61%).

**$[(CuL^3)_2][BF_4]_2$ 4.** A methanolic solution (60 $cm^3$) containing equimolar amounts (1 mmol) of proligand, $Cu(BF_4)_2\cdot H_2O$ (0.24 g) and triethylamine was heated to reflux for 2 h. The resultant warm mixture was filtered to remove residual solids. The filtrate was allowed to stand in air overnight and small green crystals were deposited (0.23 g, 49%).

**$[CuL^3(O_2CC_6H_4NO_2\text{-}p)]$ 5.** The compound $Cu(O_2CC_6H_4\text{-}NO_2\text{-}p)_2$ (1 mmol, 0.23 g) in MeOH (30 $cm^3$) was stirred and heated to reflux. A methanolic solution (10 $cm^3$) containing proligand (1 mmol) and triethylamine (1 mmol) was added. The green mixture was refluxed for 1 h. After cooling, the solution was filtered to remove residual solids and the filtrate allowed to stand in air for a few days. A green crystalline solid was collected (0.22 g, 42%).

**$[(CuL^6)_2][SO_4]$ 6.** An equimolar amount of triethylamine (1 mmol) was added dropwise to a methanolic solution (50 $cm^3$) containing proligand (0.35 g) and $CuSO_4$ (0.17 g). A fresh green precipitate emerged immediately. The mixture was stirred and heated for 2 h. After cooling the suspension was filtered to yield a solid, which was recrystallised from water–EtOH (1:1), 0.22 g (44%).

**$[CuL^6(O_2CMe)]\cdot H_2O$ 7.** The complex was prepared in the same way as for **1**, 0.29 g (60%). Recrystallisation from methanol–acetone (1:10) gave dark blue crystals suitable for X-ray crystallographic analysis.

**$[CuL^6(O_2CPh)]$ 8.** The complex was prepared in the same way as for **1**, 0.20 g (42%). In the recrystallisation of the resultant solid, tetrahydrofuran was used instead of ethyl acetate.

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

### X-Ray crystallography

**Complex 1.** *Crystal data.* $C_{27}H_{35}CuN_4O_7$, $M = 564.09$, crystallises from methanol–ethyl acetate as blue oblongs, crystal dimensions 0.72 × 0.30 × 0.30 mm, monoclinic, space group $P2_1/c$ ($C^5_{2h}$, no. 14), $a = 8.907(4)$, $b = 16.016(6)$, $c = 18.441(6)$ Å, $\beta = 94.84(3)°$, $U = 2621(2)$ Å$^3$, $Z = 4$, $D_c = 1.429$ g $cm^{-3}$, Mo-Kα radiation ($\bar{\lambda} = 0.710\,73$ Å), μ(Mo-Kα) = 0.884 $mm^{-1}$, $F(000) = 1188$.

Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the ω-scan method. Of the 4067 reflections measured, all of which were corrected for Lorentz-polarisation effects (but not for absorption), 2058 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. 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. Refinement converged at a final $R = 0.0634$ ($wR2 = 0.1849$ for all 2987 data, 324 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 −0.668 and 0.874 e Å$^{-3}$. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0948P)^2 + 4.421P]$ 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 SHELXL 93[7] as implemented on a Viglen 486dx computer.

**Complex 7.** *Crystal data.* $C_{21}H_{22}CuN_4O_6$; $M = 489.97$, crystallises from methanol–acetone as blue blocks; crystal dimensions 0.66 × 0.45 × 0.22 mm, monoclinic, space group $C2/c$, $a = 13.452(2)$, $b = 7.971(3)$, $c = 40.123(5)$ Å, $\beta = 96.890(10)°$, $U = 4271(2)$ Å$^3$, $Z = 8$, $D_c = 1.524$ g $cm^{-3}$, μ(Mo-$K_\alpha$) = 1.069 $mm^{-1}$, $F(000) = 2024$.

Three-dimensional, room temperature X-ray data were collected as before. Of the 3761 reflections measured, corrected as for complex **1**, 2503 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved and refined as for **1**. Refinement converged at $R = 0.0427$ ($wR2 = 0.1259$, for all 2784 data, 284 parameters, mean and maximum δ/σ 0.000, 0.000). Minimum and maximum final electron density −0.540 and 0.777 e Å$^{-3}$. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 15.1124P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/52.

## Results and Discussion

### Synthesis and characterisation of the complexes

The copper(II) complexes are readily obtained using complexation reactions between the proligands and the appropriate copper(II) salts in the presence of triethylamine;[1,3] dimeric compounds are formed when $Cu(ClO_4)_2$, $Cu(BF_4)_2$ or $CuSO_4$ are used in the reaction. The synthesis and characterisation of the complexes $[(CuL^2)_2][ClO_4]_2{\cdot}H_2O$ **9** and $[CuL^2(O_2CBu^t)]{\cdot}H_2O$ **10** have been reported by us previously.[1] The IR spectra of the complexes show characteristic bands for the three anions. Acetate, pivalate, benzoate and *p*-nitrobenzoate have been used to prepare mononuclear carboxylate-containing complexes. In their IR spectra the antisymmetric and symmetric stretching bands of benzoate occur at 1561 and 1361 $cm^{-1}$ and, due to the effect of the electron-withdrawing $NO_2$ group, the antisymmetric band for the nitrobenzoate is found at 1519 $cm^{-1}$.

The principal peaks in the positive-ion fast-atom bombardment (FAB) spectra of the complexes followed the pattern established previously.[1] For compounds **3**, **4** and **6** a molecular ion peak was found corresponding to the dinuclear fragment $[Cu_2L_2X]^+$ whereas for the carboxylato-complexes the molecular ion peak corresponded to a mononuclear fragment $[CuL]^+$. Electronic spectral data for all the present complexes are summarised in Table 2. The principal absorbance bands are similar to those found for the closely related square-planar complexes previously reported.[1,3] The low-energy absorptions displayed in the spectra of the dimeric complexes **3**, **4** and **6** suggest the presence of a more trigonal-bipyramidal element in their geometry in solution.[8]

### Crystal structures of complexes 1, 3 and 7

The reaction of copper(II) pivalate and proligand $HL^5$, capable of producing a 5,6,6-membered chelate ring sequence at the copper, gave a green-blue crystalline product, **1**, the IR spectrum of which is very similar to that of complex **10**. The crystal structure of complex **1**, recrystallised from an acetonitrile–ethyl acetate mixture, was solved and shows a dramatic difference from the structures of complexes derived from related heteroleptic tripodal ligands capable of producing 6,6,6-membered chelate ring sequences at copper. The phenolate oxygen atom is now co-ordinated to the square-pyramidal copper atom at the axial position. The molecular structure of the complex is shown in Fig. 2 and selected bond

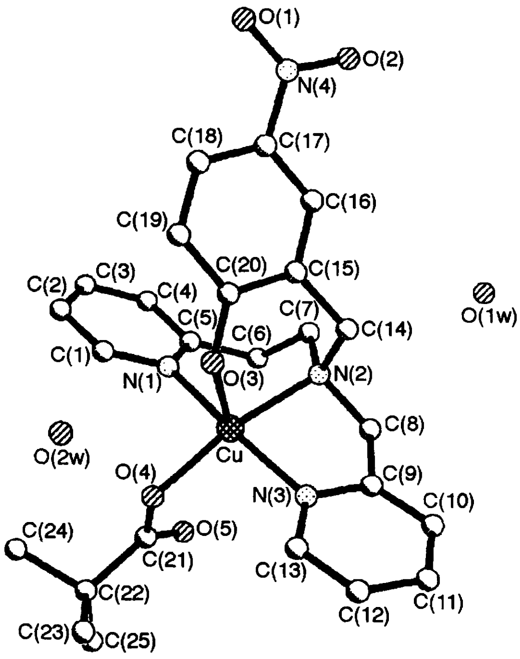

**Fig. 2** Molecular structure of complex **1**

**Table 1** Elemental analyses with calculated values in parentheses and mass spectral data for the complexes

| Compound | Analysis (%) C | H | N | *m/z* for $M^+$ |
|---|---|---|---|---|
| **1** $[CuL^5(O_2CBu^t)]{\cdot}MeCN$ | 57.10 (57.00) | 5.35 (5.50) | 12.45 (12.30) | 426 |
| **2** $[CuL^5(O_2CMe)]$ | 52.65 (52.45) | 4.75 (4.80) | 11.40 (11.15) | 427 |
| **3** $[(CuL^3)_2][ClO_4]_2{\cdot}H_2O$ | 48.00 (47.90) | 3.95 (4.00) | 8.80 (8.80) | 835 |
| **4** $[(CuL^3)_2][BF_4]_2$ | 49.80 (50.20) | 3.90 (4.00) | 9.30 (9.25) | 822 |
| **5** $[CuL^3(O_2CC_6H_4NO_2\text{-}p)]$ | 58.15 (58.50) | 4.30 (4.15) | 10.25 (10.50) | 367 |
| **6** $[(CuL^6)_2][SO_4]$ | 54.65 (54.95) | 4.65 (4.35) | 10.40 (10.10) | 921 |
| **7** $[CuL^6(O_2CMe)]{\cdot}H_2O$ | 51.75 (51.50) | 4.55 (4.55) | 11.45 (11.45) | 412 |
| **8** $[CuL^6(O_2CPh)]$ | 58.40 (58.55) | 3.90 (4.15) | 10.30 (10.50) | 413 |

**Table 2** Electronic spectra (λ/nm, ε/$dm^3$ $mol^{-1}$ $cm^{-1}$) for the complexes in MeCN

| Compound | Ligand based[a] | Charge transfer[a] | | Ligand field[b] |
|---|---|---|---|---|
| **1**[c] | 257 (12 000) | 404 (23 500) | | 645 (140) |
| **2** | 256 (14 200) | 405 (18 600) | | 669 (210) |
| **3**[d] | 257 (11 200) | | | 839 (190) |
| | 291 (sh) (6 150) | | | |
| **4**[d] | 257 (12 000) | | | 840 (200) |
| | 290 (sh) (6 500) | | | |
| **5** | 264 (22 100) | | | 669 (90) |
| **6**[d,e] | 252 (8 250) | 391 (10 850) | | 794 (120) |
| | 257 (11 750) | 402 (20 600) | | 690 (130) |
| **7** | 256 (11 200) | 401 (17 650) | | 685 (140) |
| **8** | 257 (12 600) | | 438 (600) | 780 (140) |
| **9**[c,d] | 287 (sh) (64 000) | | | |
| | 253 (12 900) | | 460 (400) | 670 (110) |
| **10**[c] | 300 (sh) (4 300) | | | |

[a] ≈1.0 × $10^{-4}$ mol $dm^{-3}$. [b] 1.5 × $10^{-3}$ mol $dm^{-3}$. [c] Data taken from ref. 1. [d] Concentrations based on the monomer. [e] In water.

**Table 3** Selected bond lengths (Å) and angles (°) for the complexes $[\mathrm{CuL^5(O_2CBu^t)}]\cdot\mathrm{MeCN}$ **1**, $[\mathrm{(CuL_3)_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O}$ **3** and $[\mathrm{CuL^6(O_2CMe)}]\cdot\mathrm{H_2O}$ **7**

(*a*) $[\mathrm{CuL^5(O_2CBu^t)}]\cdot\mathrm{MeCN}$ **1**

| | | | |
|---|---|---|---|
| Cu–O(4) | 1.957(5) | Cu–N(1) | 2.014(6) |
| Cu–N(3) | 2.015(6) | Cu–N(2) | 2.075(6) |
| Cu–O(3) | 2.176(5) | | |
| O(4)–Cu–N(1) | 92.3(2) | O(4)–Cu–N(3) | 92.7(2) |
| N(1)–Cu–N(3) | 169.3(3) | O(4)–Cu–N(2) | 169.0(2) |
| N(1)–Cu–N(2) | 92.5(2) | N(3)–Cu–N(2) | 81.1(2) |
| O(4)–Cu–O(3) | 96.5(2) | N(1)–Cu–O(3) | 91.7(2) |
| N(3)–Cu–O(3) | 97.1(2) | N(2)–Cu–O(3) | 93.2(2) |

(*b*) $[\mathrm{(CuL^3)_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O}$ **3**

| | | | |
|---|---|---|---|
| Cu(1)–O(1) | 2.177(9) | Cu(1)–N(2) | 2.054(11) |
| Cu(1)–O(1A) | 1.952(9) | Cu(1)–N(3) | 1.992(11) |
| Cu(1)–N(1) | 2.026(12) | | |
| O(1)–Cu(1)–N(1) | 105.3(4) | O(1)–Cu(1)–N(2) | 91.1(4) |
| N(1)–Cu(1)–N(2) | 82.9(5) | O(1)–Cu(1)–N(3) | 99.0(4) |
| N(1)–Cu(1)–N(3) | 152.3(5) | N(2)–Cu(1)–N(3) | 83.6(4) |
| O(1)–Cu(1)–O(1a) | 80.6(3) | N(1)–Cu(1)–O(1a) | 102.4(4) |
| N(2)–Cu(1)–O(1a) | 171.1(4) | N(3)–Cu(1)–O(1a) | 94.4(4) |

(*c*) $[\mathrm{CuL^6(O_2CMe)}]\cdot\mathrm{H_2O}$ **7**

| | | | |
|---|---|---|---|
| Cu–O(2) | 1.955(3) | Cu–N(1) | 1.981(3) |
| Cu–N(3) | 1.995(3) | Cu–N(2) | 2.060(3) |
| Cu–O(1) | 2.216(3) | | |
| O(2)–Cu–N(1) | 95.64(13) | O(2)–Cu–N(3) | 96.66(13) |
| N(1)–Cu–N(3) | 161.00(14) | O(2)–Cu–N(2) | 171.32(13) |
| N(1)–Cu–N(2) | 82.74(13) | N(3)–Cu–N(2) | 82.92(13) |
| O(2)–Cu–O(1) | 96.34(12) | N(1)–Cu–O(3) | 102.69(13) |
| N(3)–Cu–O(1) | 90.29(13) | N(2)–Cu–O(3) | 92.33(12) |

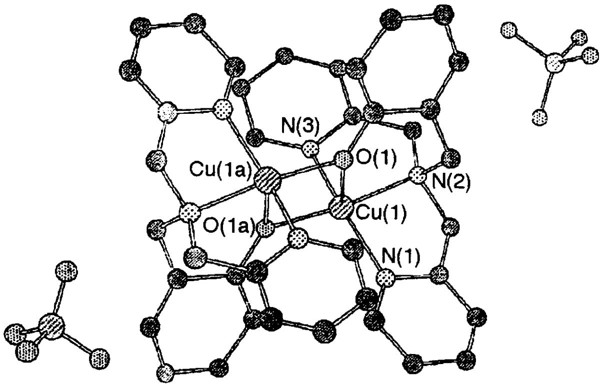

**Fig. 3** Molecular structure of complex **3**

lengths and angles, with standard deviations, are given in Table 3.

The asymmetric unit is composed of one mononuclear copper(II) complex molecule and one acetonitrile solvent molecule. The copper atom is bonded to the four donor atoms provided by the deprotonated proligand $\mathrm{HL^5}$ and to one oxygen atom of the pivalate anion in an approximately square-pyramidal co-ordination environment. One tertiary nitrogen atom, two pyridine nitrogen atoms and one pivalate oxygen atom provide the basal plane. The nitrogen atom of the pyridine ring giving a six-membered chelate ring on co-ordination is in the basal plane whilst the phenolate group twists such that the phenolate oxygen atom occupies the axial site at a distance of 2.176 Å. The copper atom lies 0.134 Å above this basal plane in the direction of phenolate oxygen. The pivalate group is regarded as monodentate with a supplementary long Cu–O interaction from the second oxygen atom.

This structure reinforces the view that steric factors, the flexibility of the ligand pendant arms, can contribute to changes in donor atom positions within given structural geometries derived from tripodal ligands. Accordingly, it can be proposed that those complexes derived from heteroleptic ligands, in this case bearing pyridinyl and phenolic arms, which are capable of forming 5,6,6- or 5,5,6-membered chelate ring sequences at the metal should have an axial oxygen–copper(II) bond in their square-pyramidal co-ordination. In order to demonstrate that this is independent of the presence of an electron-withdrawing $\mathrm{NO_2}$ group situated on the phenol, attempts were made to grow crystals of a potential mononuclear complex derived from proligand $\mathrm{HL^3}$. Although these attempts were unsuccessful crystals were obtained of the dimeric complex **3** derived from proligand $\mathrm{HL^3}$ and copper(II) perchlorate. The structure proved difficult to refine to an acceptable level ($R = 0.0869$) because of twinning problems but the gross stereochemical features are clearly identified.*

The molecular structure of complex **3** is shown in Fig. 3; selected bond lengths and angles are given in Table 3. The complex is a dimer in the solid state and the molecular dication is centrosymmetric. The copper atom is co-ordinated by two pyridine nitrogen atoms, the tertiary amine nitrogen atom and two phenolate oxygen atoms which also co-ordinate to the second copper in the dimer (Cu–O 1.981 and 2.178 Å). The copper–copper separation is 3.153 Å. The geometry at each copper atom is best described as distorted square pyramidal with a small trigonal-bipyramidal component, $\tau = 0.31$ [$\tau$ is an index of the degree of trigonality within the structural continuum between square planar and trigonal-bipyramidal geometries; for perfect square planar and trigonal-bipyramidal geometries the values of $\tau$ are zero and unity respectively. $\tau = (\beta - \alpha)/60$, where $\beta$ = N(2)–Cu(1)–O(1a) 171.1° and $\alpha$ = N(1)–Cu(1)–N(3) 152.3°].[10] The basal plane comprises two pyridine nitrogen atoms, one tertiary amine nitrogen atom and a phenolate oxygen atom from the adjacent unit in the dimer. The copper atom is 0.287 Å above the plane and is axially co-ordinated to the phenolate oxygen atom from the directly bound tripodal ligand [Cu–O(3) 2.177 Å]. The two parts of the dimer in the complex are *trans* to each other.

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* Crystal data: $\mathrm{C_{38}H_{36}Cl_2Cu_2N_6O_{10}}$, $M = 934.74$, crystallises from methanol as dark green, thick plates; crystal dimensions 0.40 × 0.55 × 0.80 mm, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, $C^5_{2h}$, no. 14), $a = 17.329(29)$, $b = 9.826(16)$, $c = 11.406(3)$ Å, $\beta = 104.75(2)°$, $U = 1878(4)$ Å$^3$, $Z = 2$, $D_c = 1.653$ g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 13.44 cm$^{-1}$, $F(000) = 955.80$. Three-dimensional, room temperature X-ray data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 two-circle diffractometer by the $\omega$-scan method, using a twinned crystal mounted along the unit-cell $c$ axis. The nature of the twinning permitted unambiguous resolution of those diffraction maxima lying on layers $l = 2, 6, 7, 11$; consequently, the relative intensities of the two twin components (the 'twin factor') could be accurately measured. On those layers for which almost perfect overlap (in $\omega$) of diffraction maxima occurred ($l = 0, 4, 9$) a composite intensity was measured by ensuring a wide scan range, and the pairs of composite measurements were deconvoluted into individual intensity measurements, using the twin factor: where only one member of the composite pair appeared above the background, both reflections were rejected. Where $\omega$ separation of diffraction maxima was uncomfortably close (within $\approx 0.2$ reciprocal lattice spacings in $a^*$ ), as appeared on layers $l = 1, 3, 5, 8, 10, 12, 13$, scans were made in the quadrants which yielded the best $\omega$ separation; those reflections still deemed to be suspect were rejected. The resulting 1861 independent reflections (of $\approx 3812$ measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz-polarisation effects, and for absorption by Gaussian integration methods (minimum and maximum transmission coefficients 0.36 and 0.58). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at $R = 0.0869$ (262 parameters, mean and maximum $\delta/\sigma$ 0.007, 0.044), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron densities were $-0.76$ and $+1.02$ e Å$^{-3}$. A unit weighting scheme was used throughout the refinement. Complex scattering factors were taken from the program package SHELXTL[9] as implemented on a Data General DG30 computer.

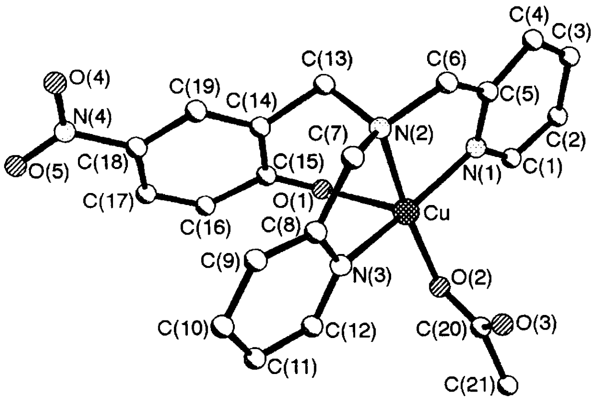

**Fig. 4** Molecular structure of complex **7**

The geometric structure of complex **3** demonstrates further that the formation of an axial phenolate oxygen–copper bond is related to steric factors arising from ligand flexibility as a 5,5,6-membered chelate ring sequence is present at the metal. It has been proposed that apical co-ordination of a phenolate was due to the introduction of the electron-withdrawing $NO_2$ group *para* to the phenolic group. In this case there is no substituent on the phenol and so this adds to the argument against any electronegative effect arising from the $NO_2$ substituent solely directing the apical occupation. Although the complexes are prepared and crystallised under very similar conditions, it would appear that by changing the number of $CH_2$ spacers in the ligand pendant arms such that 5,5,6- and 5,6,6-membered chelate ring sequences are present rather than a 6,6,6-membered one molecular structures can arise incorporating a phenolate oxygen–copper axial bond.

Deriving from this observation consideration has been given to the generation of mononuclear copper(II) complexes having a square-pyramidal co-ordination geometry in which a phenolate oxygen atom occupies the axial site and an acetate anion co-ordinates equatorially to the copper atom; such complexes could provide a synthetic model for features of the metallobiosite in GOase. Complexes **2** and **7**, derived from the reaction of copper(II) acetate with proligands $HL^5$ and $HL^6$, were synthesised and **7** was analysed by X-ray crystallography.

The crystal structure of complex **7** shows that it contains a mononuclear asymmetric unit and a water molecule. The molecular structure is shown in Fig. 4 and selected bond lengths and angles, with standard deviations, are given in Table 3. The copper(II) atom is co-ordinated to two pyridine nitrogen atoms, a tertiary amine nitrogen atom and a phenolate oxygen atom from the tetradentate ligand. Five-co-ordination is achieved through monodentate ligation to the acetate anion. The copper co-ordination geometry is almost an ideal square-based pyramid. Atoms O(2), N(1), N(2) and N(3) make up the basal plane and the phenolate oxygen atom, O(1), occupies the axial position in the co-ordination sphere. The copper lies 0.18 Å above this basal plane in the direction of O(1). In the basal plane, N(1) is *trans* to N(3) [N(1)–Cu–N(3) 161.0(1)°] and O(2) is *trans* to N(2) [O(2)–Cu–N(2) 171.32(13)°]. Equatorial copper–ligand bond lengths are 1.955–2.060 Å while the axial bond length is Cu–O(1) 2.216(3)°. The acetate group is monodentate with Cu–O(2) 1.955 Å; shorter than that found in the complex $[CuL^4(O_2CMe)]$,[3] and the second oxygen atom of the acetate is directed towards the copper at a longer separation of 2.754 Å. The solvent water molecule is hydrogen bonded to the co-ordinated phenolate oxygen.

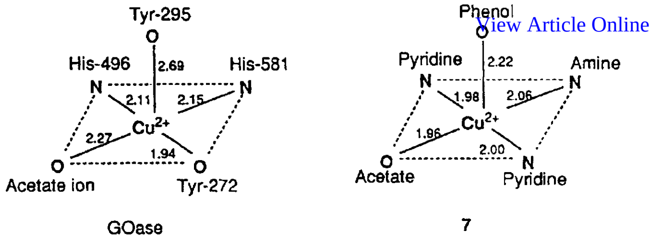

**Fig. 5** Comparison of copper(II) co-ordination environments

The above experiments demonstrate a synthetic strategy and procedure for the preparation of a synthetic model compound for the active site in galactose oxidase. The features so far reproduced (Fig. 5), in complex **7**, are the mononuclear, five-co-ordinate square-pyramidal geometry about $Cu^{II}$, the axial phenolate oxygen–copper(II) bond and the equatorial acetate–copper(II) interaction.

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