Control of the Stereochemistry of Four-co-ordinate Copper(II) Complexes by Pyridinecarboxamide Ligands: Crystal Structure, Spectral and Redox Properties†

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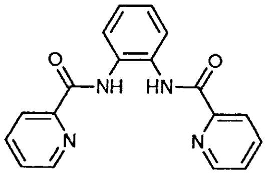
Three copper(II) complexes [CuL^1]·H$_2$O **1**, [CuL$^2{}_2$] **2** and [CuL$^3{}_2$] **3** [H$_2$L^1 = *N,N'*-*o*-phenylenebis(pyridine-2-carboxamide); HL^2 = *N*-phenylpyridine-2-carboxamide; HL^3 = *N*-2,4,5-trichlorophenylpyridine-2-carboxamide] have been prepared and their stereochemical properties investigated. Complex **2** has been characterized by X-ray crystallography: space group *P*2$_1$/*n*, *a* = 10.853(4), *b* = 19.015(6), *c* = 10.293(3) Å, β = 105.22(3)°, *Z* = 4, *R* = 0.030, *R'* = 0.034 for 2938 observed reflections. Compared to the known square-pyramidal structure of **1** it is revealed that the deprotonated bidentate ligand L^2 exerts a measurable degree of geometric control over the co-ordination sphere of **2** (distorted towards tetrahedral). Similar effects are also observed from absorption and EPR spectral results. The Cu^{II}–Cu^I redox potentials in dimethylformamide solution have been determined by cyclic voltammetry. Upon replacement of the tetradentate L^1 ligand by two uninegative bidentate L^2 or L^3 ligands, of similar donor set, a marked positive shift (*ca.* 0.6–0.7 V) was observed, implying the predominance of structural effects.

In order to evaluate the ability of bi- and tetra-dentate pyridinecarboxamide ligands[1–5] to modulate the structural and electronic properties of transition-metal centres, we have chosen complexes of copper(II) as a test case. The deprotonated ligands chosen in this work L^1–L^3 afford an especially nice opportunity to tune the stereochemistry at the copper(II) centre without changing the number, gross identity or electronic properties of the donor atoms. An additional reason derives from the current interest in copper bleomycin complexes.[6] The metal binding site in the latter contains[6d] the core donors of imidazole, deprotonated amide nitrogen, pyrimidine (pyridine N) and secondary amine joined to a terminal primary amine. Thus the present ligands partially fulfil these ligating sites.

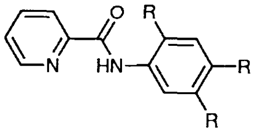
To reveal the stereochemical changes around the copper(II) centre caused by ligand-structure modification upon changing from L^1 to L^2 to L^3, we have determined the crystal structure of a representative bis(ligand) complex, [CuL$^2{}_2$], having the well known CuN$_4$ co-ordination unit.[7] As the crystal structure of [CuL^1]·H$_2$O is known (a square-based pyramid),[2b] the present investigation neatly demonstrates the structural effect on the electronic properties of CuN$_4$ units.

Experimental

Chemicals and Starting Materials.—All chemicals and solvents were of reagent grade used without further purification unless stated otherwise. Acetonitrile, chloroform, dimethylformamide (dmf), methanol and pyridine were purified/dried as previously described.[4a,8] Aniline was vacuum distilled before use. Dimethyl sulfoxide (dmso) was purified by distillation over BaO. Tetrabutylammonium perchlorate was prepared as reported previously.[4a] 2,4,5-Trichloronitrobenzene from Aldrich was used as received. Dinitrogen was purified by bubbling it through an alkaline dithionite reducing solution.



H$_2$L^1



HL^2 R = H
HL^3 R = Cl

Synthesis of Ligands.—The ligand H$_2$L^1 was synthesised as before.[9] The synthesis of HL^2 is reported in the literature.[10] However, we have developed a straightforward procedure for HL^2 and HL^3 by modifying the reported procedure of H$_2$L^1.

N-*Phenylpyridine*-2-*carboxamide* (HL^2). The ligand was prepared by adding a solution of aniline (5 g, 0.054 mol) in pyridine (7 cm^3) dropwise to a stirred solution of pyridine-2-carboxylic acid (5.75 g, 0.047 mol) in pyridine (8 cm^3) at room temperature. The resulting solution was stirred for 15 min and afterwards the temperature was gradually increased to *ca.* 100 °C using a water-bath. To this solution triphenyl phosphite (14.2 g, 0.046 mol) was added dropwise with stirring. Heating and stirring were continued for 5 h. The pyridine was then distilled off using a rotary evaporator. The resulting oil was dissolved in chloroform (20 cm^3), washed three times with water, four times with saturated sodium hydrogencarbonate solution, and then again three times with water. The resulting CHCl$_3$ solution was evaporated *in vacuo* and an oil resulted which was washed with water several times to remove unreacted aniline. The solid thus obtained was recrystallised from CHCl$_3$–

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: G = 10^{-4} T.

hexane to give a white crystalline powder of HL^2 (yield *ca.* 65%), m.p. 76 °C.[10] ^1H NMR ($CDCl_3$): δ 7.28 (m) and 7.84 (t) (7 H), 8.29 (d, 1 H), 8.57 (d, 1 H) and 10.0 (br, 1 H). IR: ν(N–H) 3335, ν(amide I) 1671 cm^{-1}.

2,4,5-*Trichloroaniline*. Solid tin(II) chloride (23 g, 0.10 mol) was added slowly to a stirred mixture of 2,4,5-trichloronitrobenzene (7 g, 0.03 mmol) and concentrated HCl (75 cm^3). The solution was boiled for 3–4 h and cooled to room temperature. A solution of NaOH (50 g in 100 cm^3) was added slowly with stirring. The mixture was warmed and filtered through a Buchner funnel and washed with water (50 cm^3). The solid thus obtained was recrystallised from aqueous methanol. The product was dried *in vacuo* (yield *ca.* 90%), m.p. 93 °C. ^1H NMR ($CDCl_3$): δ 4.1 (s, 2 H), 6.81 (s, 1 H) and 7.23 (s, 1 H).

N-2,4,5-*Trichlorophenylpyridine*-2-*carboxamide* (HL^3). Triphenyl phosphite (8 g, 25.78 mol) was added dropwise to a stirred warm solution of pyridine-2-carboxylic acid (3.1 g, 25.18 mol) and 2,4,5-trichloroaniline (5 g, 25.45 mmol) in pyridine (25 cm^3). The resulting solution was heated to *ca.* 100 °C for 4 h. The brown solution thus obtained was kept overnight at room temperature affording the product as fine needles. The product was filtered off and washed with methanol to obtain HL^3 (yield *ca.* 53%). It was recrystallised from hot methanol, m.p. 166 °C. ^1H NMR ($CDCl_3$): δ 7.50 (m, 2 H), 7.90 (t, 1 H), 8.20 (d, 1 H), 8.62 (d, 1 H), 8.86 (s, 1 H) and 10.65 (br, 1 H). IR: ν(N–H) 3320, ν(amide I) 1690 cm^{-1}.

Syntheses of Metal Complexes.—The complex $[CuL^1]\cdot H_2O$ **1** was synthesised following a reported procedure[2b] (Found: C, 54.10; H, 3.30; N, 14.30. Calc. for $C_{28}H_{14}CuN_4O_3$: C, 54.30; H, 3.00; N, 14.00%). IR: ν(amide I) 1635 cm^{-1}. EPR in dmf solution: $g_{\parallel}$ 2.191, $g_{\perp}$ 2.050, $A_{\parallel}$ 200 G at 77 K. UV/VIS (dmf), λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 660 (sh) (55), 545 (sh) (145), 382 (8000) and 302 (13 000).

$[CuL^2{}_2]$ **2**. To a solution of HL^2 (0.3 g, 1.51 mmol) in ethanol (5 cm^3) was added a solution of $CuSO_4\cdot 5H_2O$ (0.19 g, 0.76 mmol) in water (1 cm^3) and 25% ammonia solution (3 cm^3). The resulting green solution was warmed on a water-bath for 0.5 h. The precipitate which initially formed eventually dissolved and a deep green solution resulted. This was filtered and kept in the air for 4 h at room temperature. Deep green crystals which formed were filtered off and washed with a small volume of 80% ethanol. The crystals were dried *in vacuo* to give $[CuL^2{}_2]$ (yield *ca.* 72%). Recrystallisation was from aqueous methanol (Found: C, 62.50; H, 4.50; N, 12.30. Calc. for $C_{24}H_{18}CuN_4O_2$: C, 62.90; H, 4.00; N, 12.20%). IR: ν(amide I) 1632 cm^{-1}. μ_{eff} (in dmf) 1.73 μ_B. EPR in dmf solution: $g_{\parallel}$ 2.216, $g_{\perp}$ 2.055, $A_{\parallel}$ 168 G at 77 K. UV/VIS (dmf), λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 790 (sh) (110), 580 (sh) (320) and 430 (sh) (2000); (Nujol mull) 820 (sh) and 620 (sh).

$[CuL^3{}_2]$ **3**. A mixture of copper(II) acetate (90 mg, 0.45 mmol) and HL^3 (300 mg, 0.99 mmol) in methanol (7 cm^3) was stirred for 12 h at room temperature. A brown crystalline solid was obtained. It was recrystallised from $CHCl_3$–hexane and dried *in vacuo* to afford complex **3** (yield *ca.* 70%) (Found: C, 42.1; H, 2.4; N, 8.1. Calc. for $C_{24}H_{14}Cl_3CuN_4O_3$: C, 42.2; H, 2.1; N, 8.2%). IR: ν(amide I) 1632 cm^{-1}. μ_{eff} (in dmf) 1.87 μ_B. EPR in dmf solution: $g_{\parallel}$ 2.210, $g_{\perp}$ 2.055, $A_{\parallel}$ 168 G at 77 K. UV/VIS (dmf), λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 830 (sh) (60), 603 (350), 424 (1900) and 290 (sh) (13 000); (Nujol mull) 980 (sh) and 620.

Measurements.—Infrared spectra were recorded as KBr pellets on a Perkin Elmer model 1320 or 1600 Fourier-transform spectrophotometer, electronic spectra on a Perkin Elmer Lambda-2 spectrophotometer and ^1H NMR spectra of the ligands in $CDCl_3$ on a Brüker WP-80 (80 MHz) spectrometer. Chemical shifts were measured with respect to $SiMe_4$ as internal standard. Solution magnetic susceptibility measurements were done by the NMR method[11] with a PMX-60 JEOL (60 MHz) spectrometer and made use of the paramagnetic shifts of the *tert*-butyl protons of the Bu^tOH reference as the measured NMR parameter; the susceptibility of solvents[12a] and diamagnetic corrections[12b] were taken from the literature. Solution electrical conductivity measurements were done with an Elico type CM-82T conductivity bridge (Hyderabad, India) with solute concentrations of *ca.* 10^{-3} mol dm^{-3}.

X-Band EPR spectra were recorded with a Varian E-109 C spectrometer fitted with a quartz Dewar for measurements at liquid-dinitrogen temperature. The spectra were calibrated using diphenylpicrylhydrazyl, dpph (g = 2.0037).

Electrochemical experiments were performed by using a PAR model 370 electrochemistry system. All the cyclic voltammograms were recorded at a scan speed of 50 mV s^{-1} at a glassy carbon electrode. Details of the electrochemical measurements were as described earlier.[4,8] The salt $NBu^n{}_4ClO_4$ was used as supporting electrolyte (1 : 150) and all potentials were referenced to the saturated calomel electrode (SCE). The values of $E_{\frac{1}{2}}$ were taken as 0.5 (E_{pc} + E_{pa}) where E_{pc} and E_{pa} are the cathodic and anodic peak potentials respectively.

Crystal Structure Determination of $[CuL^2{}_2]$ **2**.—*Crystal data*. $C_{24}H_{18}CuN_4O_2$, M = 457.96, monoclinic, space group $P2_1/n$ (no. 14), a = 10.853(4), b = 19.015(6), c = 10.293(3) Å, β = 105.22(3)°, U = 2049(1) Å^3, D_m = 1.55 g cm^{-3}, Z = 4, D_c = 1.54 g cm^{-3}, F(000) = 980, λ(Mo-Kα) = 0.710 73 Å, μ = 11.0 cm^{-1}, crystal dimensions 0.25 × 0.42 × 0.50 mm.

Data collection and processing. A dark greenish brown block crystal was mounted on a glass fibre in a random orientation. Intensities (ω–2θ mode with $2\theta_{max}$ 50°, scan width = 0.8 + 0.350 tanθ, scan speed 1–5° min^{-1}, graphite-monochromated Mo-Kα radiation) were measured at 23 °C on an Enraf-Nonius CAD4 diffractometer (University of Louisville) and corrected for Lorentz and polarisation effects. An empirical absorption correction based on a series of scans was applied (correction factors 0.9597–0.9989, average 0.9833). Details of the experimental technique have been described elsewhere.[4c] A total of 3939 reflections were measured of which 3725 were unique, giving 2938 with $I > 3\sigma(I)$. No decay correction was applied.

Structure analysis and refinement. The structure was solved by direct methods.[13,14] Subsequent Fourier difference synthesis revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were located and their positions and isotropic thermal parameters refined. The structure was refined by a full-matrix least-squares method where the function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 4F_o{}^2/\sigma^2(F_o{}^2)$. The maximum and minimum peaks on the final Fourier-difference map corresponded to 0.30 and 0.00 e Å^{-3}, respectively. All calculations were performed using the Enraf-Nonius SDP/VAX[15] package. The final weighted R factor (on F) was 0.034 and the unweighted R factor was 0.030. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 16. The final atomic coordinates are given in Table 1.

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

Results and Discussion

The Complexes.—All the three ligands chosen in this work have two kinds of N donor atom: pyridine and peptide N. The phenyl ring in L^2 or the phenyl ring with chloro substituents in L^3 is expected to impose steric hindrance in their bis(chelate)-copper(II) complexes and that is why they were chosen.

The IR spectra of complexes **2** and **3** show the absence of ν(N–H) absorptions and a low-energy shift of the ν(amide I) absorption which indicates co-ordination of the deprotonated ligands.[2a,17] Co-ordination of water in **1** has been confirmed by X-ray structural analysis.[2b] The complexes **2** and **3** are non-conducting in dmf solution. At room temperature their effective magnetic moments in dmf solutions (Experimental section) are *ca.* 1.8, typical of $S = \frac{1}{2}$ (Cu^{II}).[18]

Table 1 Fractional atomic coordinates for non-hydrogen atoms in $[CuL^2_2]$ **2** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Cu	0.792 68(3)	0.155 75(1)	0.058 94(3)
O(1)	0.684 0(2)	−0.044 41(9)	−0.018 0(2)
O(2)	0.936 0(2)	0.351 29(9)	0.111 9(2)
N(1)	0.716 9(2)	0.105 4(1)	0.192 0(2)
N(2)	0.777 3(2)	0.064 5(1)	−0.025 3(2)
N(3)	0.774 7(2)	0.216 6(1)	−0.103 0(2)
N(4)	0.877 0(2)	0.237 7(1)	0.153 2(2)
C(1)	0.693 9(3)	0.128 2(1)	0.306 4(3)
C(2)	0.632 5(3)	0.087 5(2)	0.380 8(3)
C(3)	0.591 3(3)	0.021 9(2)	0.334 7(3)
C(4)	0.612 1(3)	−0.001 8(1)	0.216 3(3)
C(5)	0.676 4(2)	0.040 6(1)	0.147 2(3)
C(6)	0.711 6(3)	0.016 0(1)	0.022 3(3)
C(7)	0.839 0(2)	0.048 3(1)	−0.126 7(3)
C(8)	0.960 1(3)	0.074 8(2)	−0.112 8(3)
C(9)	1.026 0(3)	0.062 4(2)	−0.208 5(3)
C(10)	0.970 9(4)	0.022 6(2)	−0.319 4(3)
C(11)	0.850 8(4)	−0.003 9(2)	−0.335 6(3)
C(12)	0.783 5(3)	0.008 8(2)	−0.240 3(3)
C(13)	0.715 3(3)	0.202 7(1)	−0.231 0(3)
C(14)	0.704 6(3)	0.252 2(2)	−0.331 7(3)
C(15)	0.757 0(3)	0.317 6(2)	−0.299 1(3)
C(16)	0.818 1(3)	0.332 0(1)	−0.166 8(3)
C(17)	0.825 1(2)	0.280 8(1)	−0.070 3(3)
C(18)	0.885 3(2)	0.293 9(1)	0.076 3(3)
C(19)	0.930 0(2)	0.240 3(1)	0.294 2(3)
C(20)	0.914 4(3)	0.297 3(1)	0.373 1(3)
C(21)	0.965 0(3)	0.296 1(2)	0.510 2(3)
C(22)	1.029 3(3)	0.237 8(2)	0.572 3(3)
C(23)	1.044 7(3)	0.180 5(2)	0.495 7(3)
C(24)	0.996 0(3)	0.182 0(1)	0.357 4(3)

Crystal Structure of $[CuL^2_2]$ **2**.—A perspective drawing of the molecule together with the atom-labelling scheme is shown in Fig. 1. Table 2 contains selected bond distances and angles.

The copper(II) centre is co-ordinated by four N donor atoms, in a *trans* geometry. The average Cu-N(amide) distance (1.931 Å) is comparable to 1.933 Å in **1**.[2b] The average Cu-N(pyridine) distance lies in the typical range of 2.00–2.05 Å.[2b,6a] It is expected that the ligand dispositions around copper could be either *cis* or *trans*. However, the crystal structure reveals the *trans* geometry (Fig. 1). We believe that it is the interligand steric repulsions which preclude the *cis* geometry, as has been demonstrated in a related nickel(II) compound.[19]

The gross geometry around copper is distorted tetrahedral. The dihedral angle between the planes defined by the two CuN_2 units N(4), Cu, N(3), C(17), C(18) and N(1), Cu, N(2), C(5), C(6) is 39.78°. Thus, as expected, in complex **2** the ligand L^2 imposes distortion towards tetrahedral. A similar dihedral angle was observed with a copper(II) tropocoronand.[7g] It is to be noted here that complex **1** is a square pyramid with four nitrogens forming the plane and a water molecule in the apical position.[2b]

Stereochemical Aspects of $Cu^{II}N_4$ *Units*.—(*a*) *Absorption spectra*. In the 1000–500 nm region complexes **1**–**3** exhibit in dmf solution two shoulders of d–d origin, as revealed by their low intensities (Experimental section). The d–d absorptions of **2** and **3** are considerably red-shifted compared to those of **1**. The enhanced intensity of the former is suggestive of distortion from the tetragonal stereochemistry, caused by steric constraints. Similar enhancement of intensity due to distortion has been reported for a variety of four-co-ordinate copper(II) complexes having the CuN_4 unit.[6,7b]

Table 2 Selected bond distances (Å) and angles (°) in $[CuL^2_2]$ **2**

Cu-N(1)	2.016(2)	Cu-N(2)	1.927(2)
Cu-N(3)	1.996(2)	Cu-N(4)	1.935(2)
N(1)-Cu-N(2)	82.84(9)	N(3)-Cu-N(4)	83.22(8)
N(1)-Cu-N(3)	151.06(8)	N(2)-Cu-N(4)	157.65(9)
N(1)-Cu-N(4)	105.40(9)	N(2)-Cu-N(3)	99.66(8)

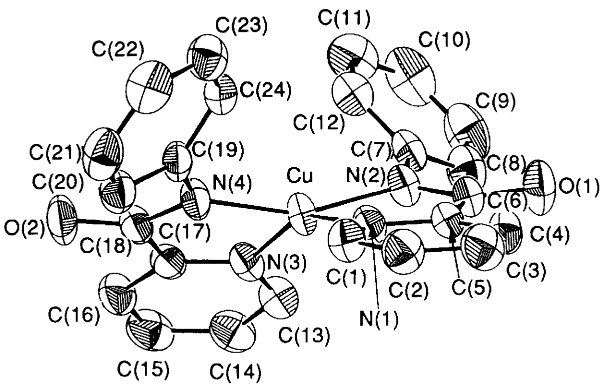

Fig. 1 The molecular structure of $[CuL^2_2]$ **2** showing the atom labelling scheme

The absorption spectra of complexes **2** and **3** dispersed in mineral oil mull exhibit (not shown) almost similar band positions to those obtained in solution (Experimental section), implying that the solid-state structures are retained in solution. The shift of the band(s) (in the region 500–1000 nm) to lower energy on going from solution to the solid state is consistent with increased axial interaction in solution at Cu^{II}.

It is interesting that the visible absorption spectrum in dmf solution of complex **3** but not **2** resembles that reported for copper(II) bleomycin[6b] even though in both **2** and **3** the copper centre is expected to have similar structure. It is thus evident that two structurally similar species **2** and **3** (see below) might exhibit different spectroscopic behaviour depending on the finer structural detail.

(*b*) *EPR spectra*. To extract complementary information on the degree of distortion towards tetrahedral in complexes **2** and **3**, EPR studies were performed. The spectra of all the complexes were recorded in dmf solution at 77 K (Fig. 2, Experimental section). The spectrum of **1** quite clearly shows superhyperfine structure (nine lines) due to four equivalent (to within the linewidth) in-plane nitrogen atoms ($A_N = 15 \times 10^{-4}\ cm^{-1}$). The data are consistent with a distorted square-pyramidal geometry (axial symmetry) about copper with an unpaired electron in the $d_{x^2-y^2}$ orbital. Complex **3** also exhibits superhyperfine structure ($A_N = 12 \times 10^{-4}\ cm^{-1}$).

The small but significant variation in $g_{\parallel}$ values obtained here provides information about distortion in the geometry around copper(II).[7b,d] This is supported by the variation in the position of the ligand-field feature; the higher $g_{\parallel}$ the lower is λ_{max}.[7b]

The value of the quotient $g_{\parallel}/A_{\parallel}$, which is a convenient empirical index[7d] of tetrahedral distortion, is 110 cm for complex **1** and 132 cm for both **2** and **3**. Thus there is an observable distortion towards tetrahedral for **2** and **3**. Additionally, from the relationship[7b] between $g_{\parallel}$ and the dihedral angle between each of the two co-ordination planes, the angles are ≈40° for **2** and **3**. This is in excellent agreement with the structural data (see above). We conclude here that the electronic structure of **3** is similar to that of **2**.

It is interesting that the EPR spectrum of complex **1** is almost identical[6a] with that of copper(II) bleomycin ($g_{\parallel} = 2.058$, $g_{\perp} = 2.213$, $A_{\parallel} = 184 \times 10^{-4}\ cm^{-1}$).

(*c*) *Copper*(II)*–copper*(I) *couple*. To identify the effect of the geometry of the $Cu^{II}N_4$ unit (see above) on the copper(II)–copper(I) redox potential, cyclic voltammetric experiments were performed. All three complexes exhibit reversible couples in dmf solution at a glassy carbon electrode. Coulometric experi-

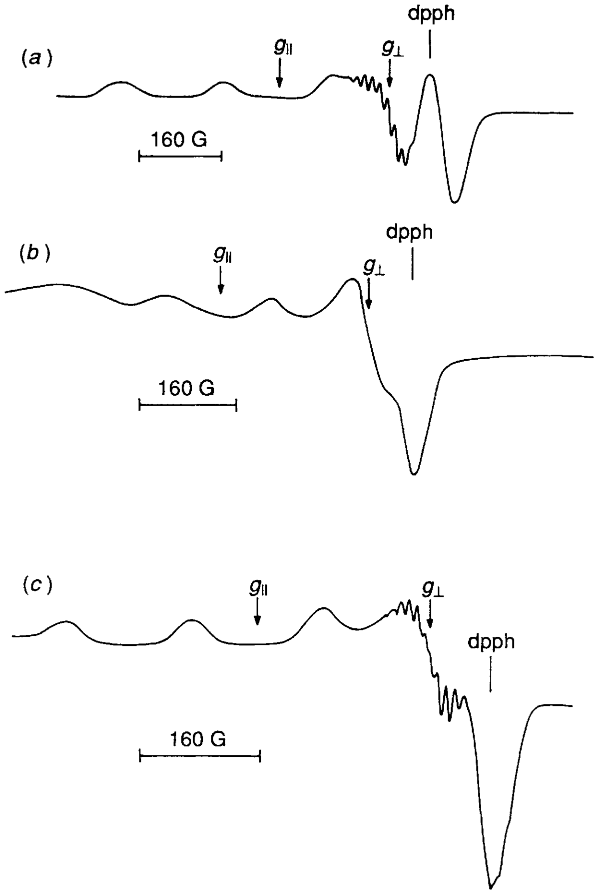

Fig. 2 The EPR spectra of (*a*) [CuL^1]·H$_2$O **1**, (*b*) [CuL^2$_2$] **2** and (*c*) [CuL^3$_2$] **3** in dmf at 77 K

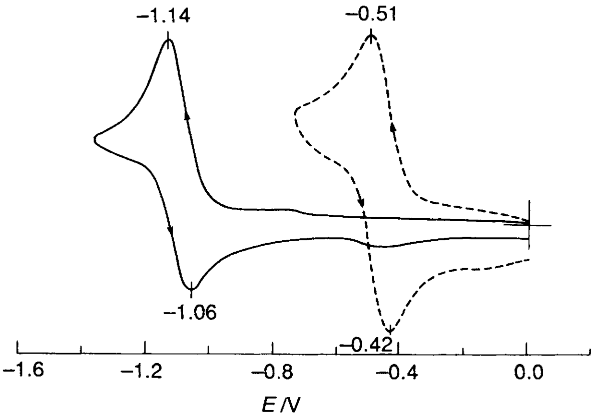

Fig. 3 Cyclic voltammograms of [CuL^1]·H$_2$O **1** (——) and [CuL^2$_2$] **2** (— — —) at concentrations of *ca.* 0.8 × 10^{-3} mol dm^{-3} in dmf (0.15 mol dm^{-3} NBu^n$_4$ClO$_4$) at a glassy carbon electrode (scan rate 50 mV s^{-1})

ments confirm the one-electron nature of the redox process. Fig. 3 reveals a substantial shift (**1**, $E_{\frac{1}{2}} = -1.10$ V, $\Delta E_p = 80$ mV; **2**, $E_{\frac{1}{2}} = -0.47$ V, $\Delta E_p = 90$ mV *vs.* SCE) of the potentials between **1** and **2** caused by the imposed distortion on the Cu^{II}N$_4$ unit. For **3** the $E_{\frac{1}{2}}$ value of this couple is -0.40 V *vs.* SCE ($\Delta E_p = 70$ mV).

The present investigation allows a reasonable comparison of the potentials of complexes **2** and **3** with that of a grossly planar compound **1**. In going from **1** to **2** or from **1** to **3** the copper(II)–copper(I) potential shifts anodically by 0.63 and 0.70 V respectively. Bearing in mind previous results due to a similar structural effect,[20,21] this is a remarkable result, showing the importance of the structural effect on the copper(II)–copper(I) redox potential for a given type of ligand system. The present shift due to the distortion of the CuN$_4$ units is most pronounced. The potentials could presumably be influenced by both ligand structural and electronic properties.

If we consider the electronic effect alone, we see that in going from complex **1** to **2** there is an additional phenyl ring in the latter complex. Such a change is not expected to affect the redox potential so drastically.[21] When the redox potentials of **2** and **3** are compared the difference is only 70 mV despite the presence of six electron-withdrawing chloride groups in **3**. Thus we conclude that the observed effect is predominantly steric (structural) in nature.

Interestingly, the reduction potentials of complexes **2** and **3** are close to the value reported for copper(II) bleomycin (−0.52 V).[6c]

Conclusion

This research has nicely demonstrated the fine tuning of stereochemistry around Cu^{II}N$_4$ centres using easily synthesisable deprotonated pyridine carboxamide ligands. The crystal structure of complex **2** reveals that, compared to tetragonal complex **1**, it is distorted towards tetrahedral. The EPR spectral results corroborate this. Cyclic voltammetric experiments neatly demonstrate the structural effect on the Cu^{II}–Cu^{I} redox potentials.

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