Structure and Properties of Copper-(II) and -(I) Complexes with 2,6-Bis[2-(thiophen-2-ylmethylimino)ethyl]pyridine†

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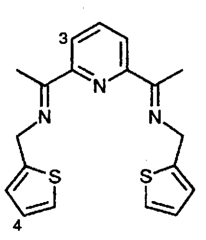
Positive-ion FAB mass spectroscopy, elemental analysis, EPR spectroscopy and X-ray diffraction analysis have revealed the structure of the copper(II) complex of 1:2 (Cu:L) stoichiometry obtained by mixing in methanol 1 equivalent of $Cu(ClO_4)_2{\cdot}6H_2O$ and 1 equivalent of 2,6-bis[2-(thiophen-2-ylmethylimino)ethyl]pyridine (L). The copper(II) ion is co-ordinated to six nitrogen atoms in an octahedral arrangement not involving the thiophene S atoms. The planes of the two *trans* pyridine subunits are perpendicular (94°); the Cu–N bond distances are 1.924 and 1.983 Å for the pyridine, 2.098, 2.118 and 2.284, 2.330 Å for the imine indicating slight distortion in the structure. Cyclic voltammetry in acetonitrile showed reversible behaviour for the $[Cu^{II}L_2]^{2+}$–$[Cu^{I}L_2]^+$ couple, and the redox potential *E* was −0.61 V *vs.* 10 mmol dm^{-3} Ag–Ag$^+$ in MeCN. Spectroscopic investigation of acetonitrile solutions having a 1:1 Cu:L molar ratio indicated the formation of species with 1:1 overall stoichiometry. The electrochemical measurements revealed that these complexes decompose during the electron transfer leading to the $[Cu^{II}L_2]^{2+}$–$[Cu^{I}L_2]^+$ redox process.

Copper proteins (blue copper proteins, superoxide dismutase, *etc.*) operate as electron-transfer systems with continual interchange between copper-(II) and -(I) redox states.[1] Current interest in copper complexes as model compounds has focused on the design and synthesis of active site mimics.[2–5] In copper proteins such as azurin[6] or plastocyanin,[7] thioether sulfur and heterocyclic nitrogen are co-ordinated to copper at the active sites. The catalytic cycle occurs *via* outer-sphere electron-transfer processes requiring co-ordination-sphere reorganization around copper. In an attempt to develop simple models towards further understanding of the structural and redox properties in copper metalloenzymes, one approach has been the design of multidentate ligands with S and N donor atoms. This paper reports a study of the copper complexes of L, 2,6-bis[2-(thiophen-2-ylmethylimino)ethyl]pyridine, a potentially pentadentate N_3S_2 ligand with two terminal thiophene S atoms. Unlike the planar 2,6-bis(iminoethyl)pyridine moiety, thiophene appears to have been rarely used in copper co-ordination chemistry.[8] The co-ordination properties with Cu^{II} and Cu^{I} have been investigated using extensive spectroscopic and electrochemical methods for evaluating the nature of the Cu–N and/or Cu–S bonds.

Experimental

Chemicals.—Preparation of L. Compound L was prepared in 80% yield by the Schiff-base condensation of 2,6-diacetylpyridine with 2-aminomethylthiophene: a solution of 2,6-diacetylpyridine (2.2 mmol) in acetonitrile (20 cm^3) was added dropwise to a solution of 2-aminomethylthiophene (4 mmol) in acetonitrile (30 cm^3) and allowed to stir with reflux for 4 h.



L

After cooling the mixture, white needles of L were obtained. IR (KBr): 1630 cm^{-1}, ν(C=N). NMR (200 MHz, $CDCl_3$): ^{1}H, δ 8.25 (2 H, d, *J* = 8.5, pyridine), 7.75 (1 H, t, *J* = 8.5 Hz, pyridine), 7.25 (2 H, m, thiophene), 7.02 (4 H, m, thiophene), 4.93 (4 H, s, CH_2) and 2.53 (6 H, s, CH_3); ^{13}C, δ 167.77 (C=N), 155.64, 143.97, 136.64 (pyridine), 126.69, 124.06, 123.63, 121.69 (thiophene), 51.35 (CH_2) and 14.4 (CH_3).

Preparation of the Copper Complexes.—In a first attempt to prepare the copper(II) complex a stoichiometric amount of solid $Cu(ClO_4)_2{\cdot}6H_2O$ (Aldrich, 0.4 mmol in 10 cm^3 methanol) was added to a methanolic solution (30 cm^3) containing L (0.4 mmol). The resulting green needles were recrystallized from acetonitrile. They were suitable for X-ray crystallography and were used in the physicochemical studies. IR (KBr): 1620 cm^{-1}, ν(C=N). Visible spectrum (in methanol): 695 nm (d–d transition). Mass spectral data and elemental analysis revealed a 1 Cu:2 L complex. Positive-ion FAB mass spectrum: *m/z* 870 (2 L + Cu + ClO_4, 869), 769 (2 L + Cu, 769.5), 516 (L + Cu + ClO_4, 516) and 416 (L + Cu, 416.5) (Found: C, 47.10; H, 3.95; Cl, 7.55; Cu, 6.55; N, 8.50; S, 12.75. $C_{38}H_{38}Cl_2CuN_6O_8S_4$ requires C, 47.10; H, 3.90; Cl, 7.35; Cu, 6.55; N, 8.65; S, 13.2%). The complex $[Cu^{II}L_2]^{2+}$ was also obtained after addition

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

of 1 equivalent of $Cu(ClO_4)_2 \cdot 6H_2O$ to 2 equivalents of L in methanol. For the copper(I) complexation study, $[Cu(MeCN)_4]ClO_4$ was prepared as described in the literature.[9] All the commercial reagents were of the highest purity and were used without purification.

X-Ray Crystallography.—The above synthesis afforded well shaped crystals suitable for an X-ray diffraction study. Preliminary Weissenberg photographs showed the monoclinic system. A crystal of approximate dimensions 0.3 × 0.2 × 0.3 mm was mounted on an Enraf-Nonius CAD-4 four-circle diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ 0.7107 Å). An intensity decay of 10% was observed over 246 h and corrected for by a linear fit. Accurate cell parameters were derived from least-squares fitting of the setting angles of 25 independent reflections. They are reported in Table 1 with other pertinent details regarding the structure determination. The space group $P2_1/a$ was ascertained from systematic absences and the data collection was performed at room temperature. The data were corrected for Lorentz and polarization factors but not for absorption.

Crystal structure determination. The structure determination was straightforward using the heavy-atom method included in the SHELX 76 package.[10] The positions of the non-hydrogen atoms were obtained from Fourier-difference maps. The thiophene groups were found to be disordered about the C–C bond which connects these groups to the main carbon framework. The disorder was such that two separate sets of atoms could be seen for each five-membered ring in a Fourier map. On the basis of the interpolated heights of the peaks for these partial atoms in the map, fixed population parameters of 0.5 were assigned for each set. These were refined with isotropic thermal parameters. In the last refinement model, hydrogen atoms were fixed at their calculated positions with isotropic thermal parameters equal to those of their parent carbon atoms.

Selected bond lengths and angles are reported in Table 2, atomic coordinates in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Spectrometry.—The EPR spectra were recorded at 100 K on a Varian E112 spectrometer operating at 9.4 GHz with diphenylpicrylhydrazyl (dpph) as an external calibrant. Proton NMR spectra of fresh solutions maintained under an argon atmosphere were recorded on an AC 200 Bruker spectrometer (working at 200.13 MHz) using a 5 mm probe at 25 °C. Chemical shifts were measured in ppm from internal $SiMe_4$. The proton resonances were assigned by using homonuclear decoupling. The concentrations of L and Cu^I were in the ranges 0.03–0.06 and 0.006–0.06 mol dm^{-3} respectively and the Cu:L ratio was varied from 0.1:1 to 2:1. Fast-atom bombardment (FAB) mass spectra in the positive mode were recorded on a Nermag R 1010C apparatus equipped with an M scan (Wallis) atom gun (8 kV, 20 μA). The complex peak intensities were normalized to the 3-nitrobenzyl alcohol matrix peak at m/z = 153.9 which was set at 100%.

Table 1 Crystal and structural refinement data for $[Cu^{II}L_2][ClO_4]_2$

Formula	$C_{38}H_{38}Cl_2CuN_6O_8S_4$
M	921.9
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	14.929(6)
b/Å	16.437(9)
c/Å	17.264(6)
β/°	95.48(1)
U/Å^3	4217.3
Z	4
μ/mm^{-1}	0.5
T/K	295
θ range/°	1–27.5
hkl ranges	−19 to 19, 0–21, 0–22
Reflections measured	10 324
No. of observed reflections [$I > 4\sigma(I)$]	4790
Refined parameters	537
$R(F_o)$	0.062
$R'(F_o)$	0.057
w	$[\sigma^2(F_o)^2]^{-1}$
Goodness of fit, S	1.21
$\Delta\rho_{min}$, $\Delta\rho_{max}$/e Å^{-3}	−0.53, 0.54
Maximum shift/error	0.61 (not disordered atoms) 1.8 (disordered atoms)

Electrochemistry.—The electrochemical behaviour of the Cu–L redox system was studied in aqueous media using 0.1 mol dm^{-3} KNO_3 as supporting electrolyte, or in acetonitrile using 0.1 mol dm^{-3} tetra-*n*-butylammonium perchlorate. Experiments were carried out using either a PAR model 273 potentiostat or a model 264 A polarographic analyser equipped with a model 303 A mercury-drop electrode. The electrochemical curves were recorded on a Kipp-Zonen *x–y* recorder. All experiments were run under an argon atmosphere at room temperature. A standard three-electrode electrochemical cell was used. Potentials are referred to a saturated calomel reference electrode (SCE) for the experiments in aqueous media or to a 10 mmol dm^{-3} Ag–Ag^+ reference electrode in acetonitrile with 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$. Potentials referenced to the Ag–Ag^+ system can be converted into the SCE by adding 0.29 V.[11] The working electrode was the mercury electrode, a vitreous carbon-disc electrode (VCE) (diameter 3 mm) or a platinum-disc electrode (diameter 5 mm) polished with 1 μm diamond paste. Rotating-disc electrode (RDE) voltammetry was performed using a Tacussel model EDI instrument. In order to prevent adsorption phenomena at the mercury electrode in aqueous media, the polarograms were recorded in solutions containing a small amount of Triton X100. The electrochemical study was performed using the isolated $[CuL_2][ClO_4]_2$ complex or mixtures of $Cu(ClO_4)_2 \cdot 6H_2O$ and L or $[Cu(MeCN)_4]ClO_4$ and L having various Cu:L ratios. No difference in the cyclic voltammograms was observed when the experiments were run in solutions prepared from $[CuL_2][ClO_4]_2$ or from a mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ + L in 1:2 ratio.

Results

Synthesis of the Copper(II) *Complexes.*—The reaction of L with solid $Cu(ClO_4)_2 \cdot 6H_2O$ in a 1:1 molar ratio in methanol yielded green needles which were recrystallized from acetonitrile. Mass spectral data [m/z = 769 (2 L + Cu) and 870 (2 L + Cu + ClO_4)] and elemental analysis revealed a complex of 1:2 (Cu:L) stoichiometry. The structure of the solid was determined by X-ray analysis. We have also investigated the co-ordination properties of L in solution by means of EPR spectroscopy and electrochemical measurements. In addition,

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu^{II}L_2][ClO_4]_2$

Cu–N(1)	1.924(4)	Cu–N(20)	2.098(4)
Cu–N(2)	1.983(5)	Cu–N(30)	2.284(4)
Cu–N(10)	2.118(4)	Cu–N(40)	2.330(4)
N(1)–Cu–N(2)	173.7(2)	N(2)–Cu–N(40)	75.6(2)
N(1)–Cu–N(10)	78.3(2)	N(10)–Cu–N(20)	156.6(2)
N(1)–Cu–N(20)	78.3(2)	N(10)–Cu–N(30)	89.3(2)
N(1)–Cu–N(30)	98.5(2)	N(10)–Cu–N(40)	96.0(2)
N(1)–Cu–N(40)	110.5(2)	N(20)–Cu–N(30)	92.3(2)
N(2)–Cu–N(10)	102.9(2)	N(20)–Cu–N(40)	93.4(2)
N(2)–Cu–N(20)	100.3(2)	N(30)–Cu–N(40)	151.0(2)
N(2)–Cu–N(30)	75.4(2)		

the complexation of Cu^I by L was studied by ^1H NMR spectroscopy.

Crystal and Molecular Structure of $[Cu^{II}L_2][ClO_4]_2$.—An ORTEP[12] projection of the compound $[Cu^{II}L_2][ClO_4]_2$, also showing the atomic numbering, is depicted in Fig. 1. The compound crystallizes in the monoclinic space group $P2_1/a$. The copper(II) ion is in a slightly distorted octahedral geometry having atoms N(30) and N(40) at the apexes. The thiophene rings are far from the copper centre which is only bonded to the three nitrogen atoms of each 2,6-bis(iminoethyl)pyridine group. The planes of the two *trans* pyridine rings are almost perpendicular (94°) and the two imine nitrogens of each ligand are roughly in the corresponding pyridine plane.

Electron Paramagnetic Resonance.—The anisotropic EPR spectrum was obtained at 100 K from a solution of the crystallized complex $[Cu^{II}L_2]^{2+}$ dissolved in methanol with 5% dimethyl sulfoxide (dmso). The spectrum [Fig. 2(*a*)] exhibited the usual line shape for mononuclear copper(II) complexes with a $d_{x^2-y^2}$ ground state. The $g_{\parallel}$ (g_z) value (2.231) was greater than $g_{\perp}$ (g_x and g_y) (2.086). The anisotropic values for g_x and g_y were not resolved and no $A_{\perp}$ hyperfine constant was observed. The $A_{\parallel}$ hyperfine constant of 138×10^{-4} cm^{-1} related to the $I_N = \frac{3}{2}$ nuclear spin of copper was measured from the splitting of the four well resolved signals. The quotient $g_{\parallel}/A_{\parallel}$ is an indication of the stereochemistry of the chelates in solution. Addison[2] has suggested that this quotient may be an empirical index of tetrahedral distortion from tetragonal geometry, *i.e.* values lower than 140 cm are observed for square-planar structures and those higher than 150 cm for tetrahedrally distorted complexes. The value of 162 cm for $[Cu^{II}L_2]^{2+}$ thus indicates a tetrahedral distortion. This is slightly different than in the solid state (tetragonal), presumably as a result of a less-constrained geometry in the frozen solution than in the solid state. It should be noted that the spectrum of a methanolic solution of 1 equivalent of copper and 1 equivalent of L shows the same signals as those in Fig. 2(*a*) corresponding to the $[Cu^{II}L_2]^{2+}$ complex.

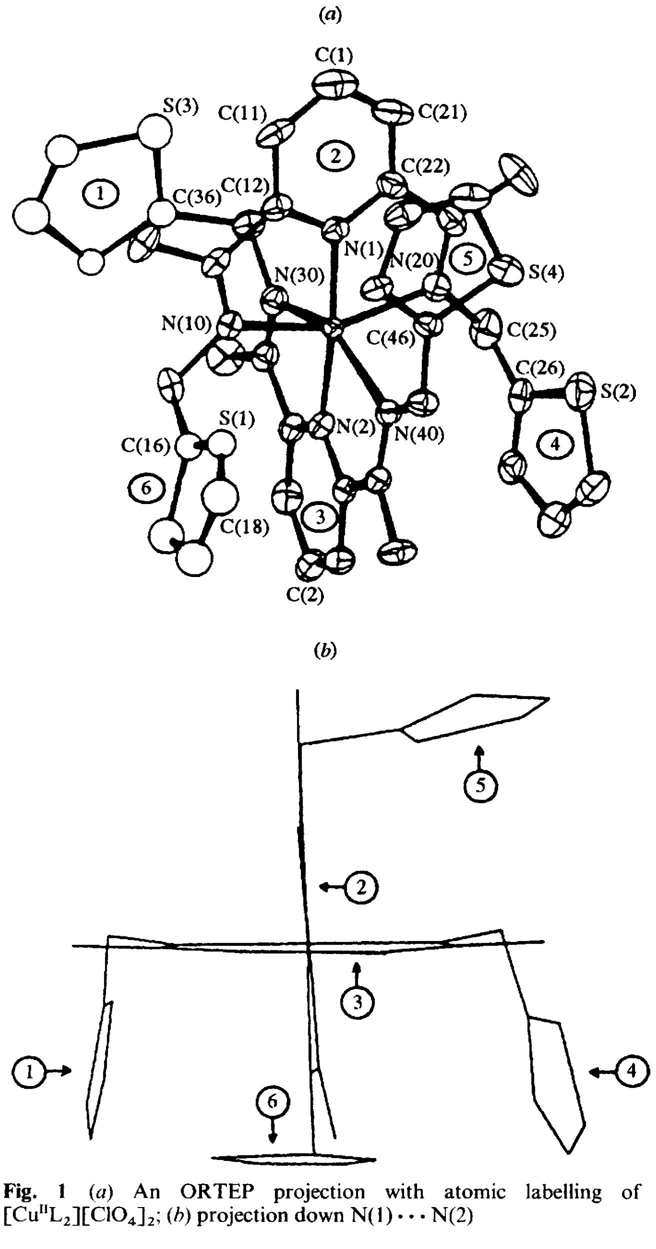

Fig. 1 (*a*) An ORTEP projection with atomic labelling of $[Cu^{II}L_2][ClO_4]_2$; (*b*) projection down N(1) ··· N(2)

Similar experiments were conducted in acetonitrile. Both the crystallized complex after dissolution in acetonitrile (with 5% dmso for an appropriate glass at 100 K) and the direct mixture of 1 equivalent of copper(II) with 2 equivalents of L, without recrystallization, exhibited the same spectra ($g_{\parallel} = 2.225$, $g_{\perp} = 2.088$, $A_{\parallel} = 138 \times 10^{-4}$ cm^{-1}, $g_{\parallel}/A_{\parallel} = 161$) as that of the $[Cu^{II}L_2]^{2+}$ complex in methanol [Fig. 2(*b*)]. In addition, the electronic spectral parameters, $\lambda_{max} = 690$ nm, $\varepsilon = 70$ dm^3 mol^{-1} cm^{-1}, are very close to those in methanol ($\lambda_{max} = 695$ nm, $\varepsilon = 67$ dm^3 mol^{-1} cm^{-1}). This indicates negligible solvent effect on the spectral characteristics of the six-co-ordinated species. However, somewhat different results from those in methanol were obtained after mixing 1 equivalent of copper(II) with 1 equivalent of L. The EPR spectrum of the solution at equilibrium [Fig. 2(*c*)] reveals for copper a slightly different environment to that in $[Cu^{II}L_2]^{2+}$ ($g_{\parallel} = 2.241$, $g_{\perp} = 2.060$, $A_{\parallel} = 159 \times 10^{-4}$ cm^{-1}, $g_{\parallel}/A_{\parallel} = 141$) indicating a rather square-planar geometry. The complex has been characterized by a 1 : 1 overall stoichiometry as deduced from positive-ion FAB mass spectroscopy: the solid extracted after evaporation of acetonitrile gave molecular-ion peaks at *m/z* 416 and 515 corresponding to $[Cu^{II}L]^{2+}$ and $[Cu^{II}L]^{2+},ClO_4^-$ species.

Electrochemistry.—A polarogram recorded for an aqueous solution containing 10^{-4} mol dm^{-3} of $[Cu^{II}L_2]^{2+}$ was

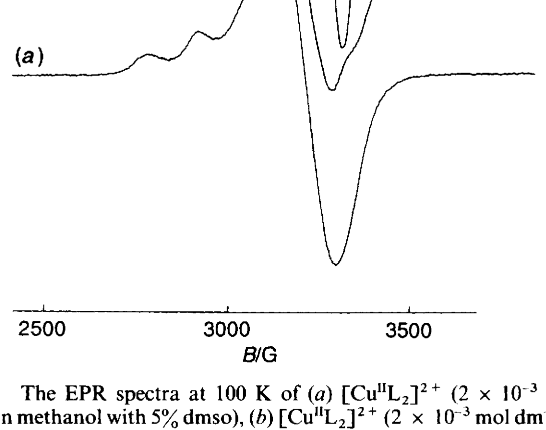

Fig. 2 The EPR spectra at 100 K of (*a*) $[Cu^{II}L_2]^{2+}$ (2×10^{-3} mol dm^{-3} in methanol with 5% dmso), (*b*) $[Cu^{II}L_2]^{2+}$ (2×10^{-3} mol dm^{-3} in acetonitrile with 5% dmso) and (*c*) a 1 : 1 Cu^{II} : L molar ratio solution in acetonitrile with 5% dmso. G = 10^{-4} T

Table 3 Atomic positional parameters (× 10^4) for $[Cu^{II}L_2][ClO_4]_2$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	8 121(0)	−35(0)	2 259(0)
S(1)	10 895(1)	1 010(1)	2 630(1)
S(2)	8 208(2)	−3 050(2)	2 954(2)
S(2′)	7 836(5)	−2 018(6)	3 991(6)
S(3)	4 958(3)	561(3)	1 759(3)
S(3′)	5 307(5)	−745(5)	1 054(4)
S(4)	9 439(1)	1 296(1)	4 172(1)
N(1)	7 455(3)	734(3)	2 817(3)
N(2)	8 694(3)	−829(3)	1 596(3)
N(10)	8 735(3)	1 077(3)	1 990(3)
N(20)	7 196(3)	−794(3)	2 749(3)
N(30)	7 271(3)	17(3)	1 088(3)
N(40)	9 344(3)	−537(3)	3 057(3)
C(1)	6 412(6)	1 873(5)	3 525(5)
C(2)	9 543(4)	−1 911(4)	647(4)
C(11)	7 096(5)	2 097(5)	3 128(4)
C(12)	7 633(4)	1 531(4)	2 768(4)
C(13)	8 398(5)	1 703(4)	2 279(4)
C(14)	8 661(6)	2 587(4)	2 159(5)
C(15)	9 457(4)	1 145(5)	1 454(4)
C(16)	10 315(4)	733(4)	1 760(4)
C(17)	10 736(4)	123(4)	1 400(4)
C(18)	11 538(5)	−119(5)	1 858(5)
C(19)	11 716(4)	288(5)	2 516(5)
C(21)	6 242(4)	1 041(5)	3 577(4)
C(22)	6 776(4)	472(4)	3 204(4)
C(23)	6 641(4)	−421(4)	3 143(4)
C(24)	5 864(4)	−802(4)	3 524(4)
C(25)	7 108(4)	−1 677(4)	2 582(4)
C(26)	7 777(8)	−2 177(8)	3 194(7)
C(27)	8 125(8)	−2 084(8)	4 000(8)
C(28)	8 531(8)	−2 604(8)	4 378(7)
C(29)	8 712(9)	−3 222(8)	3 879(9)
C(26′)	7 598(14)	−2 168(15)	3 029(13)
C(27′)	7 958(10)	−2 953(10)	2 649(10)
C(28′)	8 576(12)	−3 300(11)	3 429(12)
C(29′)	8 629(15)	−2 905(13)	4 087(13)
C(31)	8 799(4)	−1 440(4)	356(4)
C(32)	8 377(4)	−915(4)	844(4)
C(33)	7 561(4)	−439(4)	572(4)
C(34)	7 140(4)	−556(4)	−249(4)
C(35)	6 453(4)	532(4)	913(4)
C(36)	5 602(10)	−1(9)	1 195(9)
C(37)	5 283(13)	−864(11)	905(10)
C(38)	4 429(12)	−968(9)	1 448(11)
C(39)	4 252(11)	−260(9)	1 836(10)
C(36′)	5 688(10)	244(8)	1 248(10)
C(37′)	5 123(9)	880(9)	1 619(8)
C(38′)	4 369(11)	69(9)	1 870(10)
C(39′)	4 464(13)	−651(10)	1 528(11)
C(41)	9 839(4)	−1 824(4)	1 423(4)
C(42)	9 409(4)	−1 271(4)	1 883(4)
C(43)	9 719(4)	−1 119(4)	2 719(3)
C(44)	10 458(4)	−1 672(4)	3 109(4)
C(45)	9 655(4)	−374(4)	3 888(3)
C(46)	9 143(4)	281(3)	4 238(3)
C(47)	8 441(4)	176(4)	4 704(3)
C(48)	8 155(4)	938(5)	4 988(4)
C(49)	8 609(5)	1 588(5)	4 753(4)
Cl(1)	7 060(1)	−3 024(1)	311(1)
Cl(2)	3 704(1)	944(1)	4 178(1)
O(1)	6 562(3)	−3 765(3)	268(3)
O(2)	6 558(4)	−2 410(4)	476(6)
O(3)	7 715(5)	−3 083(5)	890(5)
O(4)	7 445(5)	−2 844(4)	−352(3)
O(5)	2 864(4)	1 275(4)	4 238(4)
O(6)	4 376(4)	1 447(4)	4 490(4)
O(7)	3 771(6)	209(4)	4 564(5)
O(8)	3 810(4)	752(6)	3 429(4)

characterized by two well defined cathodic waves, $E_{\frac{1}{2}} = -0.32$ and -0.91 V *vs.* SCE respectively. Comparison of the height of the first wave with that corresponding to a one-electron electrochemical process allowed us to attribute the first wave to the reduction of $[Cu^{II}L_2]^{2+}$ to $[Cu^{I}L_2]^+$. The second wave appeared notably higher and was attributed to the reduction of $[Cu^{I}L_2]^+$ to Cu^0 in addition to partial reduction of the ligand.

The electrochemical behaviour of $[Cu^{II}L_2]^{2+}$ (in the range 5×10^{-4}–10^{-2} mol dm^{-3}) solutions prepared by dissolution of crystallised $[Cu^{II}L_2][ClO_4]_2$ or from a 1:2 Cu:L molar ratio mixture was investigated in acetonitrile by rotating-disc electrode (RDE) voltammetry and cyclic voltammetry on a platinum or vitreous carbon-disc electrode. At the RDE, two cathodic waves ($E_{\frac{1}{2}} = -0.61$, -0.95 V *vs.* 10 mmol dm^{-3} Ag–Ag^+ + MeCN + 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$) were observed. An exhaustive potentiostatic electrolysis at −0.7 V gave $n = 1$ exchanged electron per Cu^{II}, corresponding to the reaction $[Cu^{II}L_2]^{2+} + e^- \longrightarrow [Cu^{I}L_2]^+$. The potential of −0.61 V which converted into the SCE scale provides the same value as that measured in aqueous solution. The second wave was related to the deposition of Cu^0. The cyclic voltammogram exhibited two cathodic peaks. When the negative sweep was limited to the first cathodic peak, on the reverse scan, the corresponding anodic peak was observed ($E_{pc} = -0.65$, $E_{pa} = -0.56$ V) [Fig. 3(*a*)]. The peak separation, $\Delta E_p = 90$ mV, remained constant for scan rates between 50 and 200 mV s^{-1} in agreement with a quasi-reversible process. Extending down the negative sweep limit to a more negative potential region (*i.e.* to the second cathodic peak) resulted on the reverse scan in the appearance of an extra anodic peak, overlapping the previous one, characteristic of the redissolution of Cu^0 [Fig. 3(*b*)].

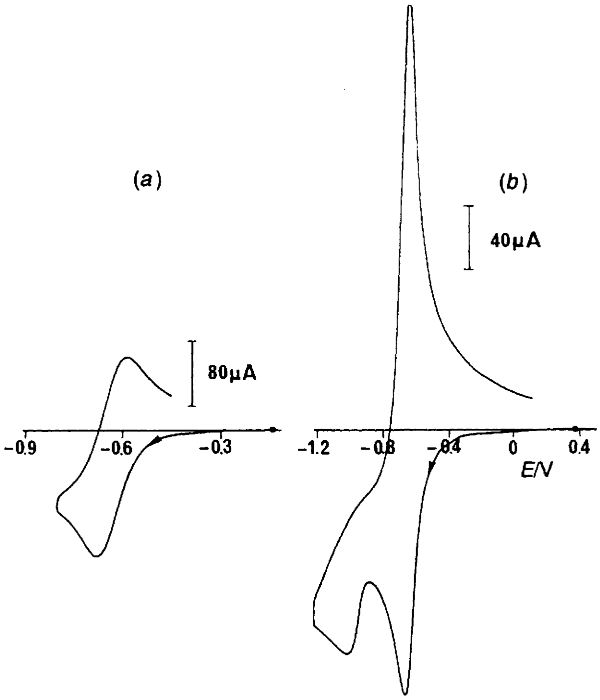

Fig. 3 Cyclic voltammetry at a platinum electrode (diameter 5 mm) in MeCN + 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ containing the isolated complex $[CuL_2][ClO_4]_2$ (3.2 mmol dm^{-3}); scan rate = 100 mV s^{-1}; *E*/V *vs.* 10 mmol dm^{-3} Ag–Ag^+ + MeCN + 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$. Scan between −0.15 and −0.80 V (*a*), or +0.40 and −1.20 V (*b*)

Cyclic voltammetry was also performed in acetonitrile solutions prepared from a mixture containing Cu^{II} and L in the molar ratio 1 : 1. After stabilization of the solution, the cyclic voltammogram exhibited [Fig. 4(*a*)] a first system in the negative region ($E_{\frac{1}{2}} = -0.07$ V) which was irreversible and a second system attributed to the $[Cu^{II}L_2]^{2+}$–$[Cu^{I}L_2]^+$ redox couple as judged by the characteristic potential. The RDE voltammogram exhibited an unique wave [$E_{\frac{1}{2}} = -0.07$ V, Fig. 4(*b*)]. An exhaustive potentiostatic electrolysis at −0.35 V gave $n = 0.5$ electron exchanged per Cu^{II}. The electrochemical curve recorded for the resulting solution showed the $[Cu^{II}L_2]^{2+}$–$[Cu^{I}L_2]^+$ system [Fig. 4(*c*)] and a poorly reversible system at positive potentials (0.80 V) characteristic of the oxidation of free Cu^{I} in acetonitrile.[11,13]

The electrochemical behaviour of acetonitrile solutions containing a mixture of Cu^{I} and L was also examined in a glove-box under argon. Whatever the Cu^{I}:L molar ratio, unexpectedly (see the NMR results), the electrochemical curves, RDE voltamperogram [Fig. 5(*a*)] and cyclic voltammogram [Fig. 5(*b*)] only exhibited the $[Cu^{I}L_2]^+$–$[Cu^{II}L_2]^{2+}$ system at −0.61 V, *i.e.* no electrochemical response of the 1 : 1 complex was observed. The UV spectrum of the solution showed absorption at $\lambda_{max} = 500$ nm ($\varepsilon = 875$ dm^3 mol^{-1} cm^{-1}). It should be pointed out that, upon exposure to air, the solution turned brown and slowly decolourized.

Complexation of Copper(I) *by* L (¹H *NMR Study*).—These NMR measurements were carried out to gain insight into the mode of co-ordination between Cu^{I} and L and to determine the stoichiometry and the stability constant(s) of the complex(es). Additions of Cu^{I} to a solution of L in CD_3CN resulted in one set of narrow signals for ligand protons according to a rapid exchange on the NMR time-scale between free and co-ordinated L. The proton chemical shifts were monitored as a function of the Cu^{I} : L molar ratio. The chemical shift variations for the various protons are shown in Fig. 6.

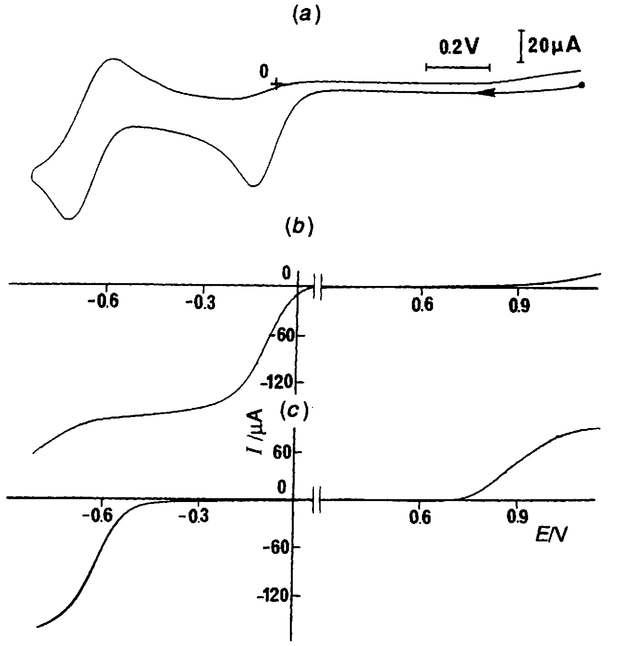

Fig. 4 Cyclic voltammetry (*a*) and voltammetry at the RDE (*b*), (*c*) in MeCN + 0.1 mol dm^{-3} $NBu^n_4ClO_4$ containing 7.7 mmol dm^{-3} $Cu(ClO_4)_2{\cdot}6H_2O$ + 7.7 mmol dm^{-3} L. Working electrode: VCE (diameter 3 mm). Scan rate = 100 (*a*) or 5 mV s^{-1} (*b*), (*c*); $N = 0$ (*a*) or 1000 revolutions min^{-1} (*b*), (*c*); *E*/V *vs.* 10 mmol dm^{-3} Ag–Ag$^+$ + MeCN + 0.1 mol dm^{-3} $NBu^n_4ClO_4$. Curves (*a*), (*b*) recorded after stabilization of the solution, (*c*) recorded after exhaustive electrolysis at −0.35 V on a platinum grid (charge passed 0.5e$^-$ per Cu)

The striking features are the singular variations for the chemical shifts of the methylene, methyl and H³ pyridine protons. The curves exhibit a minimum at Cu^{I} : L = 0.5 : 1 and a plateau for values above 1 : 1. On the other hand, a continuous decrease is exhibited for the chemical shift of the H⁴ thiophene protons until Cu^{I} : L = 1 : 1. When L is in excess (Cu^{I} : L < 0.5 : 1) these results have been interpreted in terms of the formation of the $[Cu^{I}L_2]^+$ complex. When the molar ratio Cu^{I} : L is greater than 1 : 1 another species must be considered. The NMR results are consistent with the formation of a complex having a 1 : 1 Cu : L ratio. For $[Cu^{I}L_2]^+$, the larger decrease in chemical shift for the methyl and methylene protons suggests that the imine nitrogen atoms are involved in the co-ordination around Cu^{I} providing a tetrahedral geometry. Furthermore, the continuous decrease in the chemical shift of the thiophene protons indicates that sulfur atoms are not co-ordinated to Cu in the $[Cu^{I}L_2]^+$ complex. It should be noted that only one resonance is seen for each group of protons, indicating equivalence of the two ligand molecules around the four-co-ordinated metal ion.

The addition of Cu^{I} to the $[Cu^{I}L_2]^+$ solution (Cu : L > 0.5 : 1) results in: (*i*) opposite variations of the thiophene proton chemical shifts relative to those of the other protons; (*ii*) the largest variation for the methyl chemical shift. On the other hand, the NMR spectrum exhibits only one signal for the methylene and the thiophene protons implying that the two arms of the ligand are equivalent and the molecule is symmetric or undergoes a dynamic exchange process leading to averaging

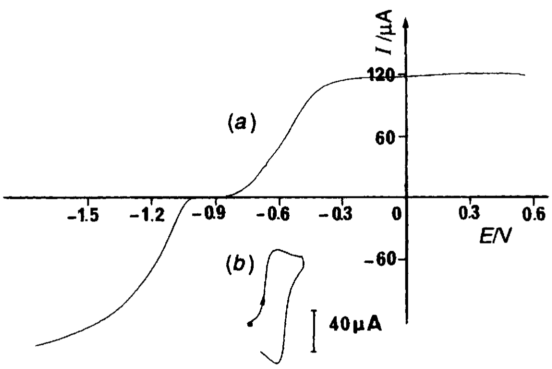

Fig. 5 Voltammetry at the RDE (*a*) and cyclic voltammetry (*b*) in MeCN + 0.1 mol dm^{-3} $NBu^n_4ClO_4$ containing 5.3 mmol dm^{-3} $[Cu(MeCN)_4]ClO_4$ + 10.6 mmol dm^{-3} L. Working electrode: VCE (diameter 3 mm). Scan rate = 5 (*a*) or 100 mV s^{-1} (*b*); $N = 300$ (*a*) or 0 (*b*) revolutions min^{-1}

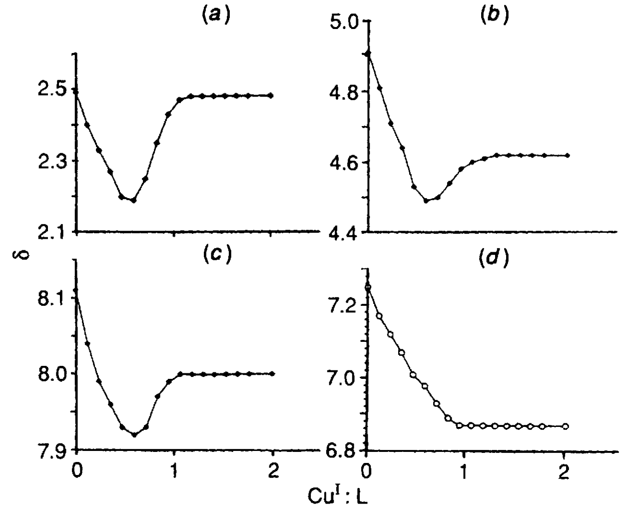

Fig. 6 Chemical shifts δ *versus* Cu^{I}:L molar ratio in CD_3CN solutions: (*a*) CH_3; (*b*) CH_2; (*c*) H³ of pyridine; and (*d*) H⁴ of thiophene

within the thiophene sub-units. The most probable occurrence is the formation of a $[Cu_2L_2]^{2+}$ species, as it will be shown in the Discussion.

The dependence of the proton chemical shifts on $[Cu]_T:[L]_T$ ratio can be quantitatively treated using equation (1) ($[Cu]_T$

$$\delta = \delta_L \frac{[L]}{[L]_T} + 2\,\delta_{CuL_2} \frac{[CuL_2]}{[L]_T} + 2\,\delta_{Cu_2L_2} \frac{[Cu_2L_2]}{[L]_T} \quad (1)$$

and $[L]_T$ are the initial concentrations) where δ is the observed proton chemical shift in a mixture of L, $[CuL_2]^+$ and $[Cu_2L_2]^{2+}$, and δ_L, δ_{CuL_2} and $\delta_{Cu_2L_2}$ are the proton chemical shifts of the corresponding species. The concentrations of L, $[CuL_2]^+$ and $[Cu_2L_2]^{2+}$ are expressed as a function of $[L]_T$, $[Cu]_T$, K_1 and K_2 according to the mass-balance equations for $[Cu]_T$ and $[L]_T$ and the reactions (2) and (3). Their

$$Cu^+ + 2\,L \xrightleftharpoons{K_1\ (\text{or}\ \beta_{120})} [CuL_2]^+ \quad (2)$$

$$[CuL_2]^+ + Cu^+ \xrightleftharpoons{K_2} [Cu_2L_2]^{2+} \quad (3)$$

values were refined by non-linear least-squares analysis minimizing the value of the residual $Q = \Sigma\,(\delta_{calc} - \delta_{exptl})^2$. The computations yield $K_1 (= \beta_{120}) = 7.66 \times 10^8$ dm^6 mol^{-2} and $K_2 = 1.83 \times 10^4$ dm^3 mol^{-1}. The cumulative constants for the formation of $[CuL_2]^+$ are $\log \beta_{120} = 8.88$ and $\log \beta_{220} = 13.15$ where β_{mlh} is defined as the equilibrium constant for the reaction $m\text{M} + l\text{L} + h\text{H} \rightleftharpoons \text{M}_m\text{L}_l\text{H}_h$.

Discussion

Some comments on the slightly distorted octahedral geometry of the $[Cu^{II}L_2][ClO_4]_2$ complex and comparison with literature data can be made. The most striking feature of this structure is that the Cu–N bond distances markedly differ for the two ligand molecules. The Cu–N bond distances for the pyridine are 1.924 and 1.983 Å. For the imine the Cu–N values are 2.098, 2.118 and 2.284, 2.330 Å. The shorter distances are very close to those determined for copper(II) complexes with ligands containing a 2,6-bis(iminoethyl)pyridine group.[14–18] For comparison, literature values are collected in Table 4 together with some Cu^I–N distances. In our case, elongation of Cu–N(30) and Cu–N(40) (2.284 and 2.330 Å respectively) is probably due to a tetragonal Jahn–Teller distortion leading to an increase in the Cu–N (pyridine) distance [Cu–N(2) 1.983 Å] in the same ligand.

The EPR and electrochemical data give information on the co-ordination properties of L in methanol and acetonitrile with copper-(II) or -(I). The mixing of Cu^{II} and L leads to the preferential formation of $[Cu^{II}L_2]^{2+}$. This structure ensures an octahedral co-ordination for copper(II) and indicates that the thiophene S donor atoms do not contribute; L thus acts as a tridentate ligand towards Cu^{II}. The electrochemical behaviour of the $[Cu^{II}L_2]^{2+}$–$[Cu^IL_2]^+$ redox couple is found to be reversible. The reduction from Cu^{II} to Cu^I is expected to involve a stereochemical change from six-co-ordinate octahedral to four-co-ordinate tetrahedral. The reversibility of the couple indicates that this process implies a small internal reorganization barrier. It is suggested that the two pyridine nitrogens move away from the copper centre to provide a tetrahedral co-ordination of Cu^I with only the imine nitrogens in accordance with their soft character. The long Cu–N bonds for one ligand molecule are favourable being similar to those measured for Cu^I–N bonds in complexes with ligands of comparable structure.[17,18]

A complex having a 1:1 metal to ligand stoichiometry is observed only in acetonitrile. Unfortunately, we were unable to obtain it as crystals suitable for X-ray analysis. The electrochemical measurements have revealed that this complex decomposes during the electron transfer. Thus electron transfer at −0.07 V leads to an unstable species which is assumed to decompose rapidly into $[Cu^{II}L_2]^{2+}$ and Cu$^+$. Then, $[Cu^{II}L_2]^{2+}$ and Cu$^+$ undergo a reversible electron transfer at −0.61 and +0.80 V respectively [*cf.* Fig. 4(*c*)]. The charge balance of the electron transfer at −0.07 V is consistent with one e$^-$ exchanged per two Cu and could suggest the formation of a binuclear compound.

Table 4 Comparison of the various Cu–N distances (Å) in copper-(II) and -(I) complexes of ligands containing a 2,6-bis(iminoethyl)pyridine group

Complex *	Pyridine N	Imine N	Ref.
$[Cu^{II}(pyep)]^{2+}$	1.920	2.010 and 2.026	17
$[Cu^{I}(pyep)]^{+}$	2.094	2.240 and 2.273	17
$[Cu^{II}(imep)_2]^{2+}$	1.923	2.036 and 2.066	16
$[Cu^{I}(imep)_2]^{+}$	1.895	2.282 and 2.534	18
$[Cu^{II}L']^{2+}$	1.930	2.022 and 2.079	15
$[Cu^{I}L']^{+}$	2.103	2.279 and 2.519	14
$[Cu^{II}L_2]^{2+}$	1.924	2.098 and 2.118	This work
	1.983	2.284 and 2.330	

* pyep = 2,6-Bis[1-(2-pyridin-2-ylethylimino)ethyl]pyridine, imep = 2,6-bis[1-(2-imidazol-4-ylethylimino)ethyl]pyridine, L′ = 2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo[14.3.1]icosa-1(20),2,14,16,18-pentaene.

Proton NMR spectroscopic study provides additional information concerning the complexation of Cu^I. The ^{1}H chemical shift variations with the Cu^I:L molar ratio can be interpreted on the basis of a rapid exchange, on the NMR time-scale, of L, $[Cu^IL_2]^+$ and a species with 1:1 stoichiometry that we assumed to be $[Cu^I_2L_2]^{2+}$. This species is supposed to result from the cation–dipole interaction between the uncomplexed Cu^I and the thiophene S atoms of the free pendant arms of $[Cu^I_2L_2]^{2+}$. Indeed, thiophene S atoms have been proposed to have weak affinity for Cu^I and to give cation–dipole interaction.[8] A $[Cu^I_2L_2]^{2+}$ species including a pure four-co-ordinated Cu^I with the four imines and a Cu^I associated to two thiophene S atoms is envisaged. It is suggested that only slight structural modification occurs such as association between uncomplexed Cu^I and $[Cu^IL_2]^+$ molecules *via* interaction through their thiophene S atoms, giving rise to a very labile oligomeric structure.

Taking into account the $E_{\frac{1}{2}}$ values for the redox couples $[Cu^{II}L_2]^{2+}$–$[Cu^IL_2]^+$ ($E_c = -0.61$ V) and Cu^{II}–Cu^I ($E_f = +0.80$ V), the ratio $\beta_{120}(Cu^IL_2{}^{2+})/\beta_{120}(Cu^{II}L_2{}^{2+})$ in acetonitrile can be calculated at 298 K from equation (4) as $10^{-23.5}$.

$$E_c = E_f + 0.06 \log [\beta_{120}(Cu^IL_2{}^+)/\beta_{120}(Cu^{II}L_2{}^{2+})] \quad (4)$$

This value is indicative of a very strong stabilization of Cu^{II} relative to Cu^I in the presence of L. The stability constants $\beta_{120}(Cu^{II}L_2{}^{2+})$ of the copper(II) complex can be calculated as $10^{32.4}$ dm^6 mol^{-2} from $\beta_{120}(Cu^IL_2{}^+)$ determined by NMR spectroscopy. Therefore, L appears to be a powerful chelating agent for copper(II) in acetonitrile.

Conclusion

The combined use of X-ray diffraction, electrochemistry, EPR and ^{1}H NMR spectroscopy has allowed us to characterize and understand the co-ordination properties of a novel compound based on a 2,6-bis(iminoethyl)pyridine group and containing two thiophene subunits. The main feature of the complexation of Cu^{II} and Cu^I with L is the formation of $[Cu^{II}L_2]^{2+}$ or $[Cu^IL_2]^+$ as the most stable complexes in relation to the $(N_3)_2$ type co-ordination of L instead of the N_3S_2 expected. This can be ascribed to the weak co-ordination properties of the thiophene S donor atoms towards Cu^{II} and Cu^{I} in accordance with the complexation of Cu^{I} with 2-isopropylimino-5-methylthiophene.[8] Compound L is thus found to be a strong chelating agent of Cu^{II} through the 2,6-bis(iminoethyl)pyridine moiety, and the electrochemically reversible behaviour of $[Cu^{II}L_2]^{2+}$ is interesting in view of the biological relevance of this compound. The formation of complexes with Cu^{I} and Cu^{II} of the 1 : 1 overall stoichiometry has been demonstrated on the basis of spectroscopic results. They are found to be electrochemically unstable and to decompose during electron transfer into the species $[Cu^{II}L_2]^{2+}$ and $[Cu^{I}L_2]^{+}$ respectively.

Acknowledgements

This work was supported by a Research Grant awarded by the European Union (Grant EUREKA SODA 437). We are grateful to Laboratories Esteve (Barcelona, Spain) and Chauvin S. A. (Montpellier, France) for their financial support and interest in this work. We thank S. Vidal (Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité, Grenoble) for computation of β_{120} and β_{220} using a non-linear least-squares analysis program.

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Received 31*st October* 1994; *Paper* 4/06610C