Synthesis, Crystal Structure, and Electrochemical Properties of μ-{2,5-Bis[*N*,*N*-bis(2′-pyridylmethyl)aminomethyl]pyrazine}-bis[chlorocopper(II)] Perchlorate†

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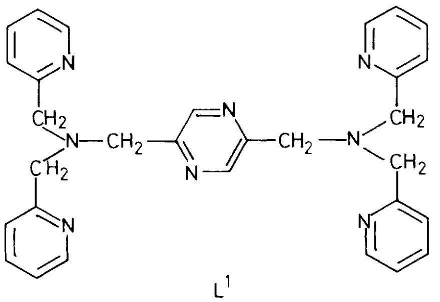
Reaction of the octadentate ligand 2,5-bis[*N*,*N*-bis(2′-pyridylmethyl)aminomethyl]pyrazine (L^1) and copper(II) chloride produces a binuclear complex, which crystallized in green (**1**) and blue (**2**) forms, $[Cu_2L^1Cl_2][ClO_4]_2 \cdot nCH_3OH$ [n = 2 for (**1**) and 0 for (**2**)]. The structures of the two complexes have been determined by *X*-ray analysis. Complex (**1**) crystallizes in the orthorhombic space group *Pcab* with a = 14.895(2), b = 19.559(3), c = 13.263(2) Å, and Z = 4, and complex (**2**) crystallizes in the triclinic space group $P\bar{1}$ with a = 10.004(1), b = 12.212(2), c = 7.791(1) Å, α = 100.99(1), β = 86.26(1), γ = 111.76(1)°, and Z = 1. The complex cations in (**1**) and (**2**) have centrosymmetric binuclear structures with copper atoms in distorted trigonal-bipyramidal and square-pyramidal geometries, respectively. The electronic spectrum in acetonitrile solution revealed that the structure in solution is the same as in complex (**1**). E.s.r. and magnetic susceptibility data for (**1**) and (**2**) show the absence of a strong magnetic interaction between the copper atoms. The compound in acetonitrile shows a quasi-reversible cyclic voltammogram which has E_{p_c} and E_{p_a} at −0.29 and −0.13 V *vs.* Ag–AgCl with shoulders observable. Controlled-potential electrolysis demonstrates that the process involves the transfer of two electrons. The two-step reduction potentials leading to Cu^{II}–Cu^{I} and Cu^{I}–Cu^{I} from Cu^{II}–Cu^{II} were estimated to be −0.14 and −0.26 V, respectively, by using the width method for the ΔE_p and $E_p - E_{p\frac{1}{2}}$ values.

In the last few years, pyrazine (pyz) bridged binuclear complexes have attracted the interest of several workers. Since Creutz and Taube[1] first reported the mixed-valence complex $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$, the nature of the metal–metal interactions through the bridged pyrazine ligand has been the main focus of attention. It is difficult to distinguish between localized and delocalized electronic structures of the mixed-valence species even in recent studies using the most sophisticated techniques available.[2] However, it is evident that electronic interaction between two metal centres through the bridged pyrazine ligand exists. Collman *et al.*[3] reported that pyrazine-bridged metalloporphyrin polymers $[\{M(oep)(pyz)\}_n]$ (M = Fe, Ru, or Os; oep = octaethylporphyrinate) are highly conductive, when partially oxidized. Magnetic interactions through the bridged pyrazine ligand were also studied in binuclear copper complexes,[4,5] and it was concluded that the direction of the magnetic orbitals relative to the bridged pyrazine ligand is important in both π and σ type exchange pathways.

This paper describes the synthesis, crystal structures, and magnetic and electrochemical properties of a pyrazine-bridged binuclear copper(II) complex bridged by the ligand 2,5-bis[*N*,*N*-bis(2′-pyridylmethyl)aminomethyl]pyrazine (L^1).

Experimental

Syntheses.—2,5-*Bis*(*bromomethyl*)*pyrazine*. A mixture of 2,5-dimethylpyrazine (3 g, 10 mmol) and *N*-bromosuccinimide (5.1 g, 28.6 mmol) in CCl_4 (200 cm^3) was refluxed for 30 min, then benzoyl peroxide (30 mg) was added. The mixture was refluxed for another 5 h and then the succinimide was filtered off. The CCl_4 solution was concentrated and chromatographed on a silica gel column with $CHCl_3$–MeOH to give white crystals (3.5 g, 30% yield). ^1H N.m.r. (400 MHz, $CDCl_3$, standard $SiMe_4$): δ 8.67 (2 H, s, 2 aryl H) and 4.55 (4 H, s, $2CH_2$).



L^1

2,5-*Bis*[N,N-*bis*(2′-*pyridylmethyl*)*aminomethyl*]*pyrazine* (L^1). A mixture of *N*,*N*-bis(2-pyridylmethyl)amine (0.2 g, 0.51 mmol) and Na_2CO_3 (0.53 g, 5 mmol) in freshly distilled acetonitrile (300 cm^3) was heated to reflux, and a solution of 2,5-bis(bromomethyl)pyrazine in acetonitrile (100 cm^3) was added dropwise over 2 h with stirring followed by refluxing for another 6 h. After cooling to room temperature, the insoluble solid was filtered off and the filtrate was evaporated to dryness. The crude product was redissolved in $CHCl_3$ and purified by alumina column chromatography with $CHCl_3$–MeOH (92:8) (3.2 g, 30% yield). ^1H N.m.r.: δ 8.69 [2 H, s, 2C(15)H], 8.52 [4 H, d, J 4.9, 2C(6)H, 2C(12)H], 7.65 [4 H, td, J 7.5, 1.5, 2C(5)H, 2C(11)H], 7.36 [4 H, d, J 7.6, 2C(3)H, 2C(9)H], 7.13 [4 H, td, J 6.3, 1.4 Hz, 2C(4)H, 2C(10)H], and 3.90 [12 H, 2C(1)H, 2C(7)H, 2C(13)H].

$[Cu_2L^1Cl_2][ClO_4]_2 \cdot 2MeOH$. Sodium perchlorate (240 mg, 0.2 mmol) in MeOH was added to a mixture of L^1 (500 mg, 0.1 mmol) and $CuCl_2 \cdot 4H_2O$ (340 mg, 0.2 mmol) in MeOH. The green precipitate was filtered off, washed with cold methanol, and dried in air (Found: C, 39.75; H, 3.65; N, 11.35. $C_{32}H_{38}Cl_4Cu_2N_8O_{10}$ requires C, 39.90; H, 3.95; N, 11.65%).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

Non-S.I. units employed: G = 10^{-4} T, e.m.u.$^{-1}$ mol = cm^{-3} mol.

Table 1. Fractional atomic co-ordinates (× 10^5 for Cu and × 10^4 for the other atoms) with estimated standard deviations (e.s.d.s) in parentheses for complex (**1**)

Atom	*x*	*y*	*z*
Cu	49 438(5)	5 840(4)	74 606(7)
Cl(1)	3 515(1)	869(1)	7 236(1)
Cl(2)	6 455(1)	1 574(1)	835(2)
N(1)	6 240(3)	220(3)	7 684(4)
N(2)	5 513(3)	1 488(3)	7 557(5)
N(3)	4 978(4)	−227(3)	6 435(4)
N(4)	4 854(3)	188(3)	9 005(4)
C(1)	6 812(5)	806(4)	8 039(6)
C(2)	6 395(5)	1 491(4)	7 775(5)
C(3)	6 885(5)	2 080(4)	7 825(6)
C(4)	6 473(6)	2 693(4)	7 663(7)
C(5)	5 564(6)	2 704(4)	7 447(7)
C(6)	5 105(5)	2 096(4)	7 387(6)
C(7)	6 547(5)	−34(4)	6 682(5)
C(8)	5 810(5)	−434(4)	6 198(5)
C(9)	5 971(6)	−990(4)	5 577(6)
C(10)	5 250(6)	−1 325(4)	5 169(7)
C(11)	4 386(6)	−1 107(4)	5 383(6)
C(12)	4 275(5)	−559(4)	6 023(6)
C(13)	6 232(5)	−330(4)	8 441(5)
C(14)	5 605(4)	−150(3)	9 283(5)
C(15)	4 255(4)	337(3)	9 724(5)
O(1)	7 254(4)	1 268(4)	480(5)
O(2)	6 244(4)	1 308(4)	1 794(5)
O(3)	6 575(4)	2 297(3)	935(6)
O(4)	5 758(4)	1 439(3)	139(5)
C(A)*	8 545(8)	2 899(5)	−248(9)
O(A)*	7 943(5)	3 330(3)	288(6)

* A denotes a solvent atom.

Table 2. Fractional atomic co-ordinates (× 10^5 for Cu and × 10^4 for the other atoms) with (e.s.d.s) in parentheses for complex (**2**)

Atom	*x*	*y*	*z*
Cu	6 432(3)	22 282(3)	44 763(4)
Cl(1)	1 555(1)	1 844(1)	1 837(1)
Cl(2)	−3 074(1)	2 857(1)	1 592(1)
N(1)	−240(2)	2 441(2)	6 927(3)
N(2)	2 518(2)	3 055(2)	5 793(3)
N(3)	−1 242(3)	824(2)	4 043(4)
N(4)	241(2)	3 937(2)	4 553(3)
C(1)	922(3)	3 094(3)	8 280(4)
C(2)	2 389(3)	3 231(2)	7 535(4)
C(3)	3 574(3)	3 617(3)	8 634(4)
C(4)	4 925(4)	3 889(3)	7 918(5)
C(5)	5 055(3)	3 775(3)	6 133(5)
C(6)	3 848(3)	3 336(3)	5 091(4)
C(7)	−1 089(4)	1 189(3)	7 178(5)
C(8)	−1 927(3)	522(3)	5 543(5)
C(9)	−3 305(4)	−325(3)	5 504(6)
C(10)	−3 974(4)	−849(3)	3 887(7)
C(11)	−3 281(4)	−560(3)	2 425(6)
C(12)	−1 876(4)	295(3)	2 500(5)
C(13)	−1 222(3)	3 100(2)	6 913(4)
C(14)	−543(3)	4 130(2)	5 950(4)
C(15)	788(3)	4 801(2)	3 603(4)
O(1)	−3 274(4)	2 439(4)	3 199(4)
O(2)*	−1 685(6)	2 763(6)	1 103(7)
O(3)*	−3 926(8)	2 168(8)	292(11)
O(4)*	−2 888(10)	3 999(6)	2 116(15)
O(2′)*	−4 178(12)	3 335(15)	1 574(14)
O(3′)*	−1 900(11)	3 833(9)	1 151(12)
O(4′)*	−3 184(18)	1 963(9)	267(12)

* Disordered atomic position with occupancy factor of 0.5.

Chloro[tris(2-pyridyl)methylamine]copper(II) *perchlorate.* [Cu(L^2)Cl][ClO_4]. This complex was prepared by the reported method.[6]

Crystal Growth.—Slow diffusion of $NaClO_4$ in MeOH into a mixture of $CuCl_2{\cdot}4H_2O$ and L^1 in MeOH gave green (**1**) and blue (**2**) tablets. Diffusion at lower temperature (*e.g.* 10 °C) tends to increase the formation of the blue species (**2**). The green and blue crystals were separated mechanically, to enable physical measurements to be made.

Physical Measurements.—Proton n.m.r. spectra were recorded on a JEOL GX400 instrument, electronic spectra on an Hitachi U-3400 spectrophotometer equipped with a reflectance attachment. E.s.r. spectra were recorded on a JEOL FE2XG, *X*-band (100-kHz field modulation) spectrometer. The microwave frequency was measured with a Takeda Riken 5201 frequency counter and the magnetic field values of the signals were measured with a Echo Denshi EFM 2000. Magnetic susceptibility on powdered samples were measured by an Oxford Faraday-type magnetic balance system equipped with a superconducting magnet. Temperature readings were calibrated with a magnetic thermometer by the use of $[Cr(NH_3)_6]Cl_3$. Cyclic voltammetry (c.v.) and constant-potential electrolysis (c.p.e.) were accomplished with a three-electrode potentiostat (Hokuto Denko HA501G potentiostat/galvanostat and HB-105 function generator, and HA-105 potentiostat/galvanostat and HF201 digital coulometer, respectively). Internal resistance drop was compensated with an Hokuto HI-203 IR compensation instrument for c.v. measurements. Electrochemical measurements were performed at 25 °C by the use of a normal three-electrode configuration consisting of a highly polished glassy carbon working electrode (area 0.79 cm^3), a platinum-wire auxiliary electrode, and a Ag–AgCl reference electrode containing saturated KCl solution (TOA Electronics Ltd., HS-205C). The reference compartment was separated from the working and auxiliary compartments of the electrochemical cell by a fritted-glass salt bridge for cyclic voltammetry. A platinum mesh for both working and auxiliary electrode was used for c.p.e. The working and auxiliary compartments contained a 0.1 mol dm^{-3} solution of the supporting electrolyte. Spectral grade acetonitrile (Dojin Lab.) was used without further purification. The supporting electrolyte NEt_4PF_6 (Fluka Chemie AG Industries) was recrystallized two times from ethanol and water, and dried under vacuum in an oven at 80 °C for 10 h. The compartment of the cell was bubbled with solvent saturated argon to deaerate the solution. Ferrocene was used as an internal standard. The correction employed an $E^{\ominus\prime}$ value for the ferrocene–ferrocenium couple of 0.400 V *vs.* n.h.e.,[7] which was assumed to be independent of the solvent. A potential for the compound is reported *vs.* corrected Ag–AgCl(aq). The potential of the ferrocene–ferrocenium couple was measured under the conditions employed: CH_3CN–NEt_4PF_6, $E^{\ominus\prime} = 0.420$ V.

Crystallography.—*Crystal data.* Green crystals of $[Cu_2L^1Cl_2][ClO_4]_2{\cdot}2MeOH$ (**1**). $C_{32}H_{38}Cl_4Cu_2N_8O_{10}$, $M = 963.63$, orthorhombic, space group *Pcab*, $a = 14.895(2)$, $b = 19.559(3)$, $c = 13.263(2)$ Å, $U = 3\,863.9(10)$ A^3, $D_m = 1.65$ g cm^{-3}, $Z = 4$, $D_c = 1.65$ g cm^{-3}, $F(000) = 1\,968$, μ(Mo-K_α) = 14.87 cm^{-1}, λ(Mo-K_α) = 0.710 73 Å.

Blue crystals of $[Cu_2L^1Cl_2][ClO_4]_2$ (**2**). $C_{30}H_{30}Cl_4Cu_2$-N_8O_8, $M = 899.52$, triclinic, space group $P\bar{1}$, $a = 10.004(1)$, $b = 12.212(2)$, $c = 7.791(1)$ Å, $\alpha = 100.99(1)$, $\beta = 86.26(1)$, $\gamma = 111.76(1)°$, $U = 867.2(2)$ Å^3, $D_m = 1.72$ g cm^{-3}, $Z = 1$, $D_c = 1.72$ g cm^{-3}, $F(000) = 456$, μ(Mo-K_α) = 16.44 cm^{-1}, λ(Mo-K_α) = 0.710 73 Å.

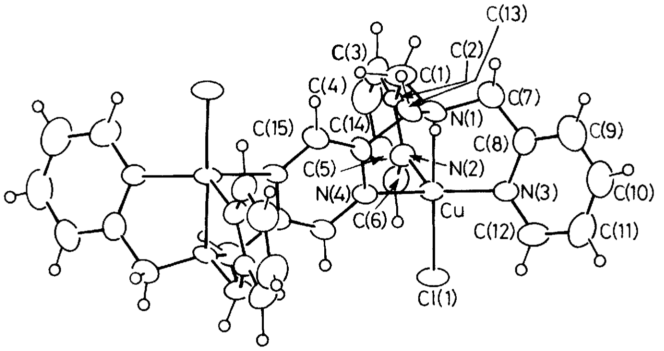

Figure 1. Molecular structure of $[Cu_2L^1Cl_2]^{2+}$ (**1**). Thermal ellipsoids are drawn at the 50% probability level

Data collection and processing. Intensity data were collected at room temperature with crystals [$0.56 \times 0.32 \times 0.12$ mm for (**1**) and $0.69 \times 0.30 \times 0.16$ mm for (**2**)] on a Rigaku AFC-5 four-circle diffractometer by use of the ω—2θ scan technique and graphite monochromated Mo-K_α radiation: 13 447 reflections ($2 < \theta < 65°$; $0 < h < 22$, $-29 < k < 29$, $0 < l < 20$) and 5 394 reflections ($2 < \theta < 60°$; $-6 < h < 6$, $-7 < k < 7$, $0 < l < 4$) were measured for (**1**) and (**2**), of which 1 612 and 2 343 were observed [$|F_o| > 3\sigma(F_o)$], respectively. The intensities were corrected for Lorentz and polarization factors and absorption, but not for extinction. Lattice constants were determined by a least-squares refinement based on 50 reflections ($13 < \theta < 15$) measured on the diffractometer.

Structure analysis and refinement. The structures were solved by the conventional heavy atom method and refined by a block-diagonal least-squares technique with anisotropic thermal parameters for non-H atoms and isotropic for H atoms. In the structure analysis of complex (**2**) a rotational disorder of the perchlorate anion around Cl–O(1) was observed and the positional and anisotropic thermal parameters of the disordered oxygen atoms were included in the refinement. Atomic scattering factors and anomalous scattering corrections were taken from ref. 8. For both refinements, a weighting scheme was chosen as $w = [\sigma^2_c + (0.030|F_o|)^2]^{-1}$ where σ^2_c was the standard deviation of $|F_o|$ calculated from counting statistics. The final R and R' values were 0.044 and 0.052 for (**1**), and 0.036 and 0.059 for (**2**). Final atomic parameters for non-hydrogen atoms are listed in Tables 1 and 2.

All the calculations were carried out on HITAC M680 computer at the Computer Centre of the Institute for Molecular Science with the program system UNICS-III.[9]

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

Results and Discussion

Description of the Structure.—Green crystals of complex (**1**) consist of $[Cu_2L^1Cl_2]^{2+}$, ClO_4^-, and methanol molecules, while the blue crystals (**2**) contain $[Cu_2L^1Cl_2]^{2+}$ and ClO_4^- only. An ORTEP drawing of the molecular structure of (**1**) is presented in Figure 1, together with the atomic labelling system; the ClO_4^- anions and methanol molecules are omitted for clarity. Selected bond lengths and angles are listed in Table 3.

Table 3. Selected bond lengths (Å) and angles (°), with e.s.d.s in parentheses for complexes (**1**) and (**2**)

	(1)	(2)
Cu–Cl(1)	2.239(2)	2.233(1)
Cu–N(1)	2.056(5)	2.062(2)
Cu–N(2)	2.028(5)	2.011(2)
Cu–N(3)	2.038(6)	2.019(2)
Cu–N(4)	2.169(5)	2.257(3)
Cl(1)–Cu–N(1)	177.9(2)	175.4(1)
Cl(1)–Cu–N(2)	98.7(2)	97.5(1)
Cl(1)–Cu–N(3)	98.2(2)	95.6(1)
Cl(1)–Cu–N(4)	99.1(1)	105.7(1)
N(1)–Cu–N(2)	83.2(2)	83.5(1)
N(1)–Cu–N(3)	80.8(2)	81.4(1)
N(1)–Cu–N(4)	79.7(2)	78.7(1)
N(2)–Cu–N(3)	134.9(2)	149.2(1)
N(2)–Cu–N(4)	105.1(2)	94.1(2)
N(3)–Cu–N(4)	113.0(2)	109.0(1)

In both crystals of (**1**) and (**2**), the cations $[Cu_2L^1Cl_2]^{2+}$ contain two five co-ordinated CuN_4Cl chromophores which are related by crystallographic centres of symmetry. Each of the Cu atoms is co-ordinated by one Cl atom and four N atoms of the ligand: two N atoms of the pyridine moiety, one N atom of pyrazine, and one N atom of amine. The co-ordination geometry around the Cu atom in (**1**) is closer to a trigonal-bipyramidal structure, while that in (**2**) is closer to a square pyramid. The angles Cl(1)–Cu–N(1) are nearly linear for both complexes [177.9(2) for (**1**) and 175.4(1)° for (**2**)]. The co-ordination angles about the Cu atoms in the plane defined by Cu, N(2), N(3), and N(4) atoms are close to the trigonal angle (120°) in complex (**1**), but deviate from this value in complex (**2**). Structural studies on mononuclear copper(II) compounds with tripod ligands[6,10,11] and a series of $[Cu(bipy)_2X]^+$ (bipy = 2,2′-bipyridine) cations have been performed.[12–14] In order to understand the electronic structure of the five-co-ordinate copper complex, it is required to analyse quantitatively the trigonality of the co-ordination geometry around the Cu atom. The distortion of the five-co-ordinate complex from ideal trigonal-bipyramidal or square-pyramidal geometries can be expressed by using an index τ introduced by Addison *et al.*,[15] which is defined as [Cl(1)–Cu–N(1) − N(2)–Cu–N(3)/60°]. The index τ is unity for the perfect trigonal-bipyramidal and zero for the square-pyramidal symmetries. The calculated τ values for (**1**) and (**2**) are 0.72 and 0.44, respectively. These results show that the CuN_4Cl chromophores in (**1**) and (**2**) are closer to trigonal-bipyramidal and square-planar symmetries, respectively, for which Cl(1)–Cu–N(1) is regarded as a principal axis of the trigonal bipyramid for (**1**), and the plane formed by Cl(1), N(1), N(2), and N(3) atoms for (**2**) is a basal plane of the square pyramid for (**2**). The deviations of the copper atoms from the basal planes [N(2)–N(3)–N(4) for (**1**) and Cl(1)–N(1)–N(2)–N(3) for (**2**)] are 0.310(4) and 0.222(1) Å, respectively. Dihedral angles between the pyrazine plane and these basal planes are 77.6(3)° for (**1**) and 106.3(3)° for (**2**). Within the CuN_4Cl chromophores of both (**1**) and (**2**), the Cu–N(4) distances are longer than the other three Cu–N bonds. These differences are, however, smaller for (**1**) than for (**2**); this causes the distortion toward the square-pyramidal geometry in (**2**). The crystallographic study shows that the methanol molecules in (**1**) do not interact with any atoms in the cation. It is thus not clear why the stereochemistries around the copper atoms is different for (**1**) and (**2**).

Electronic and Magnetic Properties.—*Optical spectra.* The electronic reflectance spectra (Figure 2) of complexes (**1**) and (**2**) are quite different. Complex (**1**) has a band maximum at 918 nm and higher-energy shoulder at 731 nm, while (**2**) has a maximum at 737 nm and lower-energy broad shoulder. Hathaway and co-workers[16] reported the assignment of electronic spectra of copper complexes with trigonal-bipyramidal and square-pyramidal geometries. By reference to this, the band at 918 nm

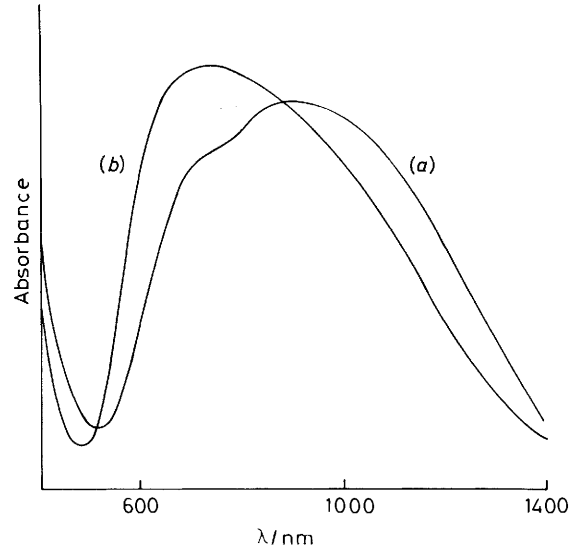

Figure 2. Electronic reflectance spectra of $[Cu_2L^1Cl_2]^{2+}$: (*a*) (**1**) and (*b*) (**2**)

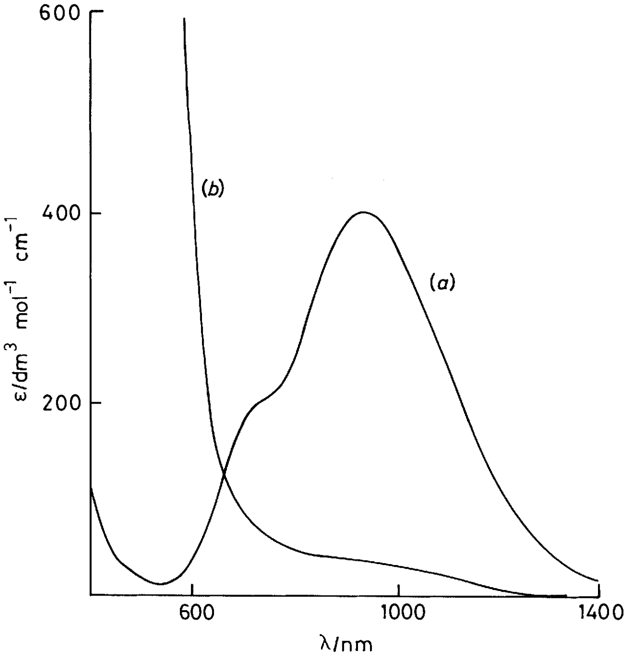

Figure 3. Electronic spectra of $[Cu_2L^1Cl_2]^{2+}$ in acetonitrile: (*a*) before electrolysis and (*b*) after electrolysis

and the shoulder at 731 nm for (**1**) can be assigned to d_{xy}, $d_{x^2-y^2} \longrightarrow d_{z^2}$ and $d_{xz},d_{yz} \longrightarrow d_{z^2}$ transitions in trigonal-bipyramidal symmetry, and the band at 737 nm and the broad low energy shoulder for (**2**) to $d_{xz},d_{yz} \longrightarrow d_{x^2-y^2}$ and $d_{z^2} \longrightarrow d_{x^2-y^2}$ mixed with $d_{xy} \longrightarrow d_{x^2-y^2}$ in the square-pyramidal system, respectively. Acetonitrile solutions of both complexes gave identical spectra [$\lambda_{max.}$ 933 (ε 409) and a shoulder band at 736 nm (ε 206 dm^3 mol^{-1} cm^{-1})] [Figure 3(*a*)], which are similar to the reflectance spectrum of (**1**). This indicates that trigonal-bipyramidal geometry is retained in solution.

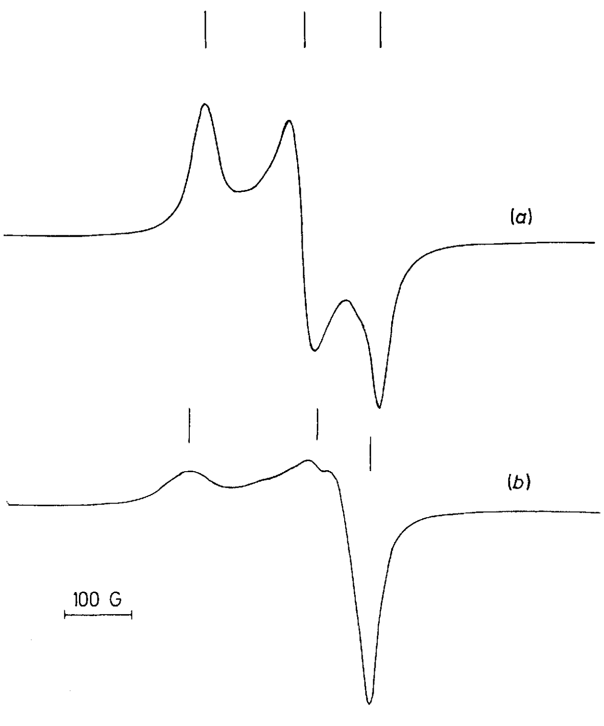

Figure 4. E.s.r. powder spectra (*X*-band at 290 K) of $[Cu_2L^1Cl_2]^{2+}$: (*a*) (**1**) and (*b*) (**2**)

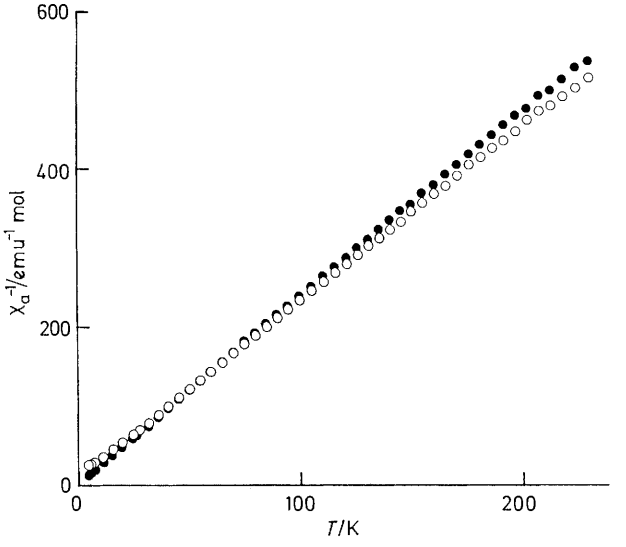

Figure 5. Magnetic susceptibility data for $[Cu_2L^1Cl_2]^{2+}$: (○) (**1**) and (●) (**2**)

E.S.R. Spectra.—The e.s.r. spectra of the five-co-ordinated copper(II) complexes show characteristic patterns according to their stereochemistry.[17] The e.s.r. spectrum [Figure 4(*a*)] of a powdered sample of (**1**) at 297 K is rhombic (g_1 = 2.037, g_2 = 2.112, and g_3 = 2.216) and consistent with a d_{z^2} ground state, *i.e.*, trigonal-bipyramidal co-ordination. On the other hand, the spectral pattern (g_1 = 2.041, g_2 = 2.093, g_3 = 2.226) [Figure 4(*b*)] of a powdered sample of (**2**) at 297 K is quite different, and interpreted as a $d_{x^2-y^2}$ ground state expected for square-pyramidal co-ordination.

Magnetic Susceptibility.—The temperature dependence of the magnetic susceptibility for complexes (**1**) and (**2**) was measured in the temperature range 4.5—230 K (Figure 5). Both sets of susceptibility data obey the Curie–Weiss law. The Curie and Weiss constants were estimated to be 0.4503 e.m.u. K mol^{-1} and −4.83 K for (**1**) and 0.4233 e.m.u. K mol^{-1} and −0.93 K for (**2**). Both the e.s.r. and magnetic susceptibility data show the

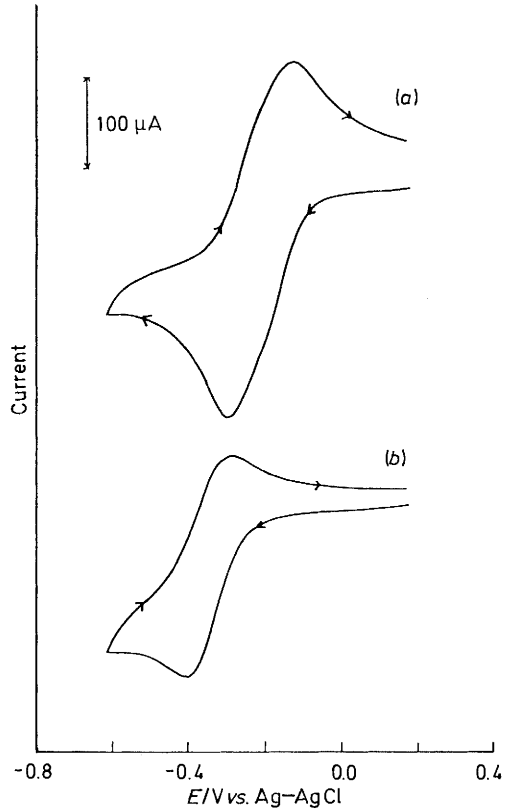

Figure 6. Cyclic voltammograms exhibited by a 1.5 × 10^{-3} mol dm^{-3} solutions of (*a*) $[Cu_2L^1Cl_2][ClO_4]_2$ and (*b*) $[CuL^2Cl][ClO_4]$ in 0.1 mol dm^{-3} NEt_4PF_6–acetonitrile at scan rates of 100 mV s^{-1} in both cases

absence of a strong magnetic interaction between the two copper atoms. It is suggested that the magnetic orbitals [d_{z^2} for (**1**) and $d_{x^2-y^2}$ for (**2**)] are perpendicular to the co-ordination bond between Cu and the N(4) atoms of the bridged pyrazine ligand, and that this results in the absence of a magnetic interaction.

Electrochemistry.—The redox properties of the binuclear copper complex $[Cu_2L^1Cl_2]^{2+}$ were studied by cyclic voltammetry (c.v.) and controlled-potential electrolysis (c.p.e.). The cyclic voltammogram [Figure 6(*a*)] for $[Cu_2L^1Cl_2]^{2+}$ in acetonitrile shows a quasi-reversible wave for which E_{p_c} and E_{p_a} are at −0.29 and −0.13 V *vs.* Ag–AgCl, respectively. Controlled-potential electrolysis was carried out at the cathodic peak potential (−0.29 V), since reduction of Cu^{2+} to copper metal occurred when c.p.e. was performed at a potential more negative than −0.29 V. C.p.e. yields a coulometric value of 1.89 electrons for this case. After the completion of the experiment, the *d–d* transition band in the electronic spectrum [Figure 3(*b*)] disappeared, indicating both copper(II) centres in the molecule were reduced to copper(I).

Concerning the redox process of this complex, it is interesting to analyse the electronic interaction between two copper centres. The cyclic voltammogram of $[Cu_2L^1Cl_2]^{+}$ in acetonitrile shows one redox peak with a shoulder. If a cyclic voltammogram for two one-electron steps shows two separate peaks with a large $\Delta E_{\frac{1}{2}}$ ($= E^1_{\frac{1}{2}} - E^2_{\frac{1}{2}} > 250$ mV) value, the $E^1_{\frac{1}{2}}$ and $E^2_{\frac{1}{2}}$ potentials [equation (1)] can be measured directly. On

$$Cu^{II}\text{–}Cu^{II} + e^- \xrightarrow{E^1_{\frac{1}{2}}} Cu^{II}\text{–}Cu^{I} + e^- \xrightarrow{E^2_{\frac{1}{2}}} Cu^{I}\text{–}Cu^{I} \quad (1)$$

the other hand, in the case of a smaller $\Delta E_{\frac{1}{2}}$ value, the wave is distorted and so direct measurement is impossible. Specifically, if $\Delta E_{\frac{1}{2}}$ is smaller than 120 mV, the two separate peaks are not resolved. Shaine, Taube, and co-workers have reported a method to determine $\Delta E_{\frac{1}{2}}$ under such circumstances, *i.e.* the individual redox potentials for multi-step redox systems.[18] Using the c.v. parameters ($\Delta E_p = 0.16$ V and $E_p - E_{p_{\frac{1}{2}}} = 0.15$ V), the potential difference $\Delta E_{\frac{1}{2}}$ and $E_{p_c} = E_{\frac{1}{2}}$ for the two-step charge-transfer reaction (1) are estimated to be −0.12 and −0.15 V, respectively.[20] Therefore, $E^1_{\frac{1}{2}}$ and $E^2_{\frac{1}{2}}$ are calculated to be −0.14 (= −0.29 + 0.15) and −0.26 (= −0.14 − 0.12 V), respectively. Redox properties have been reported for some binuclear copper(II) complexes with square-planar geometry. Lintvedt and co-workers[21–23] reported that binuclear copper(II) with 1,3,5-triketonates and their diamine Schiff-base derivatives undergo reversible transfer of one electron in the range −0.8 to −1.1 V *vs.* saturated NaCl calomel electrode. Gagné *et al.*[24,25] reported that dicopper(II) complexes with rigid square-planar symmetry were reduced quasi-reversibly in one electron steps at −0.52 and −0.91 V *vs.* n.h.e.

It should be noted that the dicopper complex studied here is reduced easily compared with the above complexes. This tendency can be interpreted as arising from the flexibility of the ligand L^1. The structure analysis of the mononuclear copper(I) complex $[CuL^3][BPh_4]$, [L^3 = tris(2-pyridyl)ethylamine] which has a tripodal ligand similar to L^1, revealed the tetrahedral co-ordination geometry around the Cu^I atom.[26] The ligand L^1 has three flexible methylene bridges per copper atom, which can easily modify the structure to tetrahedral symmetry as the complex is reduced, by contrast with the previously studied rigid square-planar dicopper complexes,[21–25] which are expected to favour Cu^{II} over Cu^I. It is also interesting to compare the electrochemical properties of related mono- and bi-nuclear copper complexes, hence the mononuclear copper(II) complex, $[CuL^2Cl]^+$,[6] which has the same co-ordination environment as $[Cu_2L^1Cl_2]^{2+}$, was prepared and re-examined. The cyclic voltammogram [Figure 6(*b*)] of $[CuL^2Cl]^+$ showed a reversible wave with the half-wave potential at −0.39 V *vs.* Ag–AgCl. This more negative reduction potential for the mononuclear system can be explained by two differences between the mono- and bi-nuclear systems. The first is the molecular charge difference.[24] It is expected that the complex with the higher molecular charge (the binuclear system) should show a higher reduction potential. The same situation has been observed for the mono- and bi-nuclear systems; $Cu^{II}(L^4)$ and $Cu^{II}Cu^{II}(L^4)^{2+}$ (L^4 = *N,N'*-disalicylidenetrimethylenediamine),[24] and $[(NH_3)_5Ru^{III}(pyz)Ru^{III}(NH_3)_5]^{6+}$ and $[Ru^{III}(NH_3)_5(pyz)]^{3+}$.[19,27] Both cases show easier reduction in the binuclear system. The second factor is the structural difference between mono- and di-copper complexes. A longer bond distance (2.169 Å) between copper and nitrogen atoms of the bridged pyrazine [Cu–N(4)] of $[Cu_2L^1Cl_2]^{2+}$ was observed, while the bond distances between copper and all nitrogen atoms in $[CuL^2Cl]^+$ range from 2.050(6) to 2.072(6) Å.[6] This causes a lower electron density on the copper atoms for $[Cu_2L^1Cl_2]^{2+}$ than for $[CuL^2Cl]^+$, hence the easier reduction for the former.

In cyclic voltammetry, multi-redox centres which are identical and non-interacting behave as a single electroactive centre but with a current magnitude corresponding to the total number of centres present. Under such circumstances, $\Delta E_{\frac{1}{2}}$ = 0.0356 V.[28] On the other hand, a conformational change such as bond breaking or rotation about a bond, taking place after the first reduction, makes addition of the second electron easier.[29] As a result, a smaller $\Delta E_{\frac{1}{2}}$ value (< 0.0356 V) will be obtained. If however the two copper atoms interact in some way such as by a magnetic superexchange mechanism, a larger $\Delta E_{\frac{1}{2}}$ value (> 0.0356 V) will be observed, and the two separate redox processes are observed.[24,25] The two copper atoms in $[Cu_2L^1Cl_2]^{2+}$ are structurally identical and magnetically noninteractive, but a two-step one-electron transfer was observed ($\Delta E_{\frac{1}{2}} = 0.12$ V). A weak interaction as discussed above, including electrostatic effects between two metal centres is thus expected.

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