DALTON
FULL PAPER

Copper(I) complexes of dinucleating macrocyclic bis(dithiadiimine) ligands

Gang Wei,[a] Geoffrey A. Lawrance,[a] David T. Richens,[b] Trevor W. Hambley[c] and Peter Turner[c]

[a] *Department of Chemistry, The University of Newcastle, Callaghan 2308, Australia*
[b] *School of Chemistry, The University of St. Andrews, The Purdie Building, St. Andrews, UK KY16 9ST*
[c] *School of Chemistry, The University of Sydney, New South Wales 2006, Australia*

The 34- and 36-membered macrocyclic bis(dithiadiimine) Schiff bases 3,17,26,40-tetrathia-6,14,29,37-tetraazapentacyclo[40.4.$1^{8,12}$.$1^{31,35}$.0.$0^{19,24}$]octatetraconta-6,8,10,12(47),13,19,21,23,29,31,33,35(48),36,42,44,46-hexadecaene (L^3) and 3,16,25,38-tetrathia-6,13,28,35-tetraazapentacyclo[38.4.$2^{8,11}$.$2^{30,33}$.0.$0^{18,23}$]octatetraconta-6,8,10,12,18,20,22,28,30,32,34,40,42,44,45(46),47(48)-hexadecaene (L^2) have been synthesized in high yield by a 2 + 2 condensation of isophthalaldehyde and terephthalaldehyde with 2,2′-*o*-phenylenebis(methylenethio)-bis(ethanamine) (L^1) in acetonitrile. Air-stable dicopper(I) complexes of L^2 and L^3 were obtained from complexation reactions with $[Cu(CH_3CN)_4]ClO_4$ in CH_3CN solution, with the structure of $[Cu_2L^2][ClO_4]_2\cdot 0.5CH_3OH\cdot 2.5H_2O$ confirmed by a crystal structure analysis. The complex consists of two N_2S_2 donor sets each tetrahedrally co-ordinated to the copper(I) ions with two *para*-substituted phenyl rings bridging the two N_2S_2 'compartments' π-stacked parallel (separation 3.5 Å), and a double helical arrangement of the ligand backbone clearly evident. Electrochemical studies of the dinuclear complexes revealed quasi-reversible Cu^I–Cu^{II} couples above +1 V (*versus* NHE), with reversibility influenced by the presence of ferrocene, which acts as a surface modifier for electron transfer.

There has been strong recent interest in helical metal complexes incorporating several metal ions in reasonably close proximity, related in part to exploration of the intrinsic chirality and shape of helicates as well as to their relevance to biological chemistry.[1–4] The biological interest is exemplified by noting that the oxygen-carrying protein haemocyanin and the tyrosinase enzyme both contain two strongly interacting copper atoms at the active site.[5] The structure and reactivity of these metalloproteins have been probed *via* a number of studies focused on synthesizing molecules with similar chromophores as models,[5–10] tied to examination of their spectroscopy and reactivity. Although the majority of helicates reported are based on polypyridine-containing open-chain ligands,[1–4,11–16] there have recently appeared examples of macrocyclic systems with a number of different donor atoms present.[17–20] These rely on inherently simple Schiff-base condensation reactions to form the required molecule.[21] Dialdehydes and diamines can react in a number of ways, either one on one (1 + 1), two of each in a concerted manner (2 + 2), or potentially in even greater self-assembly systems.[21–23] In the presence of templating metal ions, (3 + 3) and (4 + 4) condensations to produce large macrobicyclic systems have been described,[24,25] and tripodal triamines condense in the presence of Ag^I with dialdehydes in a 2 + 3 reaction.[26–29] These very large systems appear to form less readily in the absence of a metal-ion template. However, at least metal-free 2 + 2 condensations appear reasonably successful. Two new examples of 2 + 2 reactions based on an acyclic dithiadiamine ligand (L^1) are reported here.

Herein we describe the synthesis in high yield *via* the 2 + 2 condensation reaction[21–23] of terephthalaldehyde or isophthalaldehyde with 2,2′-*o*-phenylenebis(methylenethio)bis(ethanamine) (L^1) in acetonitrile of, respectively, the 36-membered macrocyclic bis(dithiadiimine) Schiff base 3,16,25,38-tetrathia-6,13,28,35-tetraazapentacyclo[38.4.$2^{8,11}$.$2^{30,33}$.0.$0^{18,23}$]octatetraconta-6,8,10,12,18,20,22,28,30,32,34,40,42,44,45(46),47(48)-hexadecaene (L^2) and the related 34-membered 3,17,26,40-tetrathia-6,14,29,37-tetraazapentacyclo[40.4.$1^{8,12}$.$1^{31,35}$.0.$0^{19,24}$]-octatetraconta-6,8,10,12(47),13,19,21,23,29,31,33,35(48),36,42,44,46-hexadecaene (L^3), along with their air-stable dicopper(I) complexes. Physical and structural properties and comparisons of the copper(I) compounds of L^2 and L^3 with analogues L^4[30] and L^5[30] are also discussed.

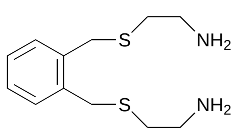
Experimental

Physical methods

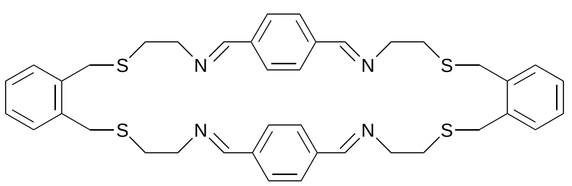
The IR spectra were recorded on a Bio-Rad FTS-7 FT-IR spectrometer with compounds dispersed in KBr discs [for the copper(I) complexes] or sandwiched between NaCl plates (for the Schiff bases). Elemental microanalyses were performed by the Microanalytical Unit, Research School of Chemistry, the Australian National University. The NMR spectra were recorded on a Bruker Avance DPX300 spectrometer in either $CDCl_3$ solution (for the Schiff bases) or $(CD_3)_2SO$ solution [for the copper(I) complexes], using the solvent as internal standard. Voltammetry in HPLC-grade CH_3CN or dried CH_3NO_2 solution (with 0.1 mol dm^{-3} tetrabutylammonium perchlorate as electrolyte and ferrocene as internal standard) employed a conventional three-electrode system and nitrogen purge gas, using a BAS model CV-27 electrochemical controller. A glassy carbon working electrode polished with alumina before measurement of each voltammogram, a Ag–AgCl reference electrode and a platinum-wire auxiliary electrode were used with the potential of ferrocene (+0.37 V *versus* NHE) as an internal standard. The potentials reported are those relative to the normal hydrogen electrode (NHE). The scan rate for cyclic voltammetry was 10 mV s^{-1}.

Crystallography

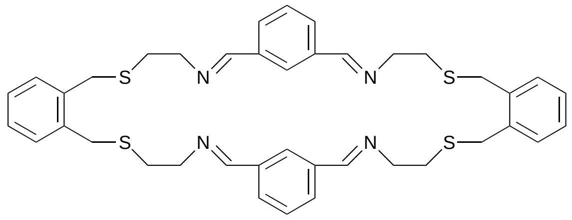
For $[Cu_2L^2][ClO_4]_2\cdot 0.5CH_3OH\cdot 2.5H_2O$, X-ray crystallographic data were collected using a Rigaku AFC7R four-circle diffractometer at 294 K. All calculations were performed using the TEXSAN[31] crystallographic software package. The structure was solved by direct methods[32] and expanded using Fourier techniques.[33] The complex straddles a two-fold axis essentially



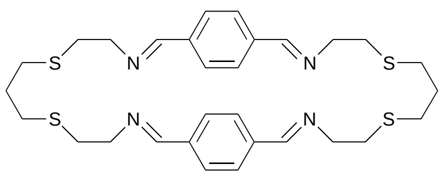
L1



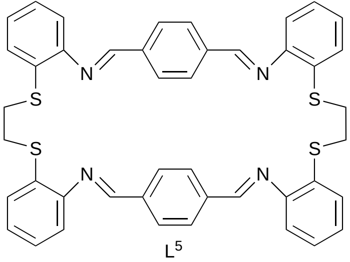
L2



L3



L4



L5

perpendicular to the Cu···Cu direction. Two sites in the asymmetric unit were refined as the oxygen atoms of water molecules, one with full occupancy and one with a 0.25 occupancy. A methanol solvate molecule was refined with an occupancy of 0.5. The carbon of the methanol molecule resides on the same two-fold axis as the complex. All of the fully occupied sites were refined on F anisotropically, and hydrogen atoms were included in a full-matrix least-squares refinement at calculated positions with group thermal parameters. No hydrogen atoms were attached to the solvate molecules, and the partially occupied non-hydrogen sites were refined isotropically.

Crystal data. $C_{40.5}H_{46}Cl_2Cu_2N_4S_4O_{11.5}$, $M = 1099.07$, monoclinic, space group $P2/n$, $a = 8.509(6)$, $b = 9.844(4)$, $c = 29.776(5)$ Å, $\beta = 95.73(4)°$, $U = 2482(2)$ Å^3, D_c ($Z = 2$) 1.471 g cm^{-3}, $F(000)$ 1130.00. Monochromatic Cu-Kα radiation, $\lambda = 1.541\,78$ Å, μ(Cu-Kα) = 41.23 cm^{-1}. Specimen 0.37 × 0.33 × 0.04 mm. The number of reflections measured was 4260 of which 3959 were unique ($R_{int} = 0.052$) and 1825 were observed. R 0.072, R' 0.065. Goodness of fit indicator 3.42. $T_{min,max}$ 0.4188, 0.8985; residual extrema +0.68, −0.43 e Å^{-3}, $w = 1/\sigma^2(F_o)$.

CCDC reference number 186/821.

See http://www.rsc.org/suppdata/dt/1998/623/ for crystallographic files in .cif format.

Syntheses

2,2′-*o*-Phenylenebis(methylenethio)bis(ethanamine) (L^1) was prepared as previously described,[34] *via* reaction of *o*-dibromoxylene with the sodium salt of 2-aminoethanethiol. The compound $[Cu(CH_3CN)_4]ClO_4$ was prepared as described elsewhere,[35] by the addition of an excess of copper powder to a known concentration of $Cu(ClO_4)_2{\cdot}6H_2O$ solution in CH_3CN under a nitrogen atmosphere. At completion of the reaction, the excess of copper powder was removed easily by filtration. Terephthalaldehyde and isophthalaldehyde are commercially available and were used as received.

3,16,25,38-Tetrathia-6,13,28,35-tetraazapentacyclo-[38.4.2^{8,11}.2^{30,33}.0.0^{18,23}]octatetraconta-6,8,10,12,18,20,22,28,30, 32,34,40,42,44,45(46),47(48)-hexadecaene (L^2). To a solution of compound L^1 (2.03 g, 7.9 mmol) in absolute ethanol (100 cm^3) was added acetonitrile (200 cm^3). The resulting solution was stirred vigorously, then a solution of terephthalaldehyde (98%, 1.08 g, 7.9 mmol) in acetonitrile (150 cm^3) was added dropwise (at the rate of *ca.* one drop every 5 s). By halfway through the addition of the latter solution the reaction mixture had become a cream suspension. After the addition was completed the suspension was stirred at room temperature (*ca.* 20 °C) overnight. Some light brown rubber-like solid at the bottom of the flask was collected and washed with a small amount of absolute ethanol and dry diethyl ether in turn, then dried in a desiccator (2.7 g, 96%). It proved spectroscopically pure. ^{1}H NMR (in $CDCl_3$): δ 8.3 (CHN), 7.7 (aryl H) and 3.9–1.8 (CH_2). ^{13}C NMR (in $CDCl_3$): δ 162.3 (N=CH), 138.7 (*C*CHN), 137.2 [(aryl) *C*CH$_2$S], 129.2 [NCHC*C*H (aryl)], 130.6 [SCH$_2$C*C*H (aryl)], 128.0 [SCH$_2$CCH*C*H (aryl)], 62.3 (NCH$_2$), 34.6 (CH$_2$*C*S) and 33.3 [S*C*H$_2$C (aryl)]. IR (NaCl plate): 1637 cm^{-1} (C=N).

3,17,26,40-Tetrathia-6,14,29,37-tetraazapentacyclo-[40.4.1^{8,12}.1^{31,35}.0.0^{19,24}]octatetraconta-6,8,10,12(47),13,19,21, 23,29,31,33,35(48),36,42,44,46-hexadecaene (L^3). A solution of compound L^1 (1.85 g, 7.2 mmol) in absolute ethanol (150 cm^3) and acetonitrile (200 cm^3) was stirred and warmed (*ca.* 40 °C) for *ca.* 20 min, cooled, then filtered to remove some insoluble light brown solid. The clear filtrate was stirred vigorously, a solution of isophthalaldehyde (98%, 0.99 g, 7.2 mmol) in CH_3CN (*ca.* 150 cm^3) was added dropwise (at the rate of *ca.* one drop every 5 s). By halfway through the addition of the latter solution the golden mixture had changed to a cream suspension. The resultant suspension was stirred at room temperature (*ca.* 20 °C) overnight. The clear liquid was decanted and the brown gum-like material collected, washed with a small amount of absolute ethanol and dry ether in turn, then dried in a vacuum desiccator (2.2 g, 86%). ^{1}H NMR (in $CDCl_3$): δ 8.4 (CHN), 7.7 (aryl H) and 3.9–1.4 (CH_2). ^{13}C NMR (in $CDCl_3$): δ 161.5 (N=CH), 137.2 (*C*CHN), 135.3 [(aryl) *C*CH$_2$S], 131.4, 130.1 [NCHC*C*H (aryl)], 128.1 [NCHCCH*C*H (aryl)], 134.3 [SCH$_2$C*C*H (aryl)], 132.0 [SCH$_2$CCH*C*H (aryl)], 62.1 (NCH$_2$), 34.7 (CH$_2$*C*S) and 33.6 [S*C*H$_2$C (aryl)]. IR (NaCl plate): 1642 cm^{-1} (C=N).

{3,16,25,38-Tetrathia-6,13,28,35-tetraazapentacyclo-[38.4.2^{8,11}.2^{30,33}.0.0^{18,23}]octatetraconta-6,8,10,12,18,20,22,28,30, 32,34,40,42,44,45(46),47(48)-hexadecaene}dicopper(I) perchlorate–hydrate (2/5), $[Cu_2L^2][ClO_4]_2{\cdot}2.5H_2O$. To a stirred solution of compound L^2 (0.31 g, 0.44 mmol) in $CHCl_3$ (300 cm^3) was added acetonitrile (200 cm^3). The solution was stirred vigorously and degassed in a nitrogen atmosphere for 1 h, and an excess of freshly prepared 0.16 mol dm^{-3} $[Cu(CH_3CN)_4]ClO_4$ (6 cm^3, 0.96 mmol) added slowly. The resulting golden solution was stirred with air excluded for *ca.* 2 h, then rotary evaporated to near dryness to yield some brown-yellow powder. Acetonitrile (*ca.* 30 cm^3) was added to redissolve the solid, and the solution filtered to remove some insoluble brown suspension. The filtrate was set aside to crystallise. After standing for a few days it was filtered to remove golden-yellow clusters of crystals, which were washed with a small amount of acetonitrile and dried in a vacuum desiccator (0.21 g, 47%). These were recrystallised further from acetonitrile–methanol to yield X-ray-quality crystals (Found: C, 44.46; H, 4.30; N, 5.18. $C_{40}H_{44}Cl_2Cu_2N_4O_8S_4\cdot2.5H_2O$ requires C, 44.48; H, 4.57; N, 5.19%). IR (KBr disc): 1624 (C=N), 3024 (aryl C–H), 776 (*o*-C–H), 815 (*p*-C–H), 1115, 624 cm^{-1} (ClO_4^-). ^1H NMR [$(CD_3)_2SO$]: δ 7.9 (CH=N), 6.6 (aryl H) and 3.7–2.6 (CH_2). ^{13}C NMR [$(CD_3)_2SO$]: δ 168.7 (N=CH), 140.3 [(aryl) *C*CHN], 138.3 [(aryl) *C*CH_2S], 131.3 [NCHC*C*H (aryl)], 135.3 [SCH_2C*C*H (aryl)], 132.2 [SCH_2CCH*C*H (aryl)], 83.3 (NCH_2), 39.2 (CH_2*C*S) and 37.9 [S*C*H_2C (aryl)]. Cyclic voltammetry: (CH_3CN solution, glassy C, 10 mV s^{-1} scan rate) $E_{\frac{1}{2}}$ ($Cu^{II/I}$) +1.03 V (Δ*E* 110 mV) (*vs.* NHE); (CH_3NO_2 solution, glassy C, 10 mV s^{-1} scan rate) $E_{\frac{1}{2}}$ ($Cu^{II/I}$) +1.24 V (Δ*E* 190 mV) (*vs.* NHE).

{3,17,26,40-Tetrathia-6,14,29,37-tetraazapentacyclo-[40.4.1^{8,12}.1^{31,35}.0.0^{19,24}]octatetraconta-6,8,10,12(47),13,19,21,23,29,31,33,35(48),36,42,44,46-hexadecaene}dicopper(I) perchlorate–hydrate, $[Cu_2L^3][ClO_4]_2\cdot H_2O$. To a stirring suspension of compound L^3 (1.3 g, 1.83 mmol) in $CHCl_3$ (200 cm^3) and acetonitrile (*ca.* 800 cm^3) further $CHCl_3$ (*ca.* 400 cm^3) was added. The resultant emulsion was degassed in a nitrogen atmosphere for *ca.* 1.5 h, and an excess of freshly prepared 0.16 mol dm^{-3} $[Cu(CH_3CN)_4]ClO_4$ (25 cm^3, 4 mmol) was added slowly. The resulting brown-yellow solution was stirred overnight protected from the atmosphere, then rotary evaporated to near dryness to yield some yellow-brownish powder which was filtered off and washed with small amounts of absolute ethanol and dry ether in turn, and dried in a vacuum desiccator (0.47 g, 25%) (Found: C, 45.69; H, 4.25; N, 5.53. $C_{40}H_{44}Cl_2Cu_2N_4O_8S_4\cdot H_2O$ requires C, 45.62; H, 4.40; N, 5.32%). IR (KBr disc): 1643 (C=N), 780 (aryl C–H), 1119, 635 cm^{-1} (ClO_4^-). ^1H NMR [$(CD_3)_2SO$]: δ 7.9 (CH=N), 6.9 (aryl H) and 3.8–1.7 (CH_2). ^{13}C NMR [$(CD_3)_2SO$]: δ 168.3 (N=CH), 138.3 [(aryl) *C*CHN], 137.4 [(aryl) *C*CH_2S], 135.3 [SCH_2C*C*H (aryl)], 135.0 [SCH_2CCH*C*H (aryl)], 134.7 [NCHC*C*H (aryl)], 132.6 [NCHCCH*C*H (aryl)], 132.2 [NCHC*C*H (aryl)], 63.7 (NCH_2), 39.3 (CH_2*C*S) and 38.1 [S*C*H_2C (aryl)]. Cyclic voltammetry: (CH_3CN solution, glassy C, 10 mV s^{-1} scan rate) $E_{\frac{1}{2}}$ ($Cu^{II/I}$) +1.10 V (Δ*E* 110 mV) (*vs.* NHE); (CH_3NO_2 solution, glassy C, 10 mV s^{-1} scan rate) $E_{\frac{1}{2}}$ ($Cu^{II/I}$) +1.20 V (Δ*E* 110 mV) (*vs.* NHE).

Results and Discussion

The bis(dithiadiimine) Schiff-base type macrocycles L^2 and L^3 with two N_2S_2 donor sets present as two linked ‘compartments’ were synthesized by employing the established 2 + 2 condensation reaction method using stoichiometric amounts of terephthalaldehyde or isophthalaldehyde with L^1 in acetonitrile. The reactions proceeded in high yields (>85%), and the products were characterised by infrared and NMR spectroscopy. Recently, the analogues L^4[30] and L^5[30] have been prepared in good yield as well by using the 2 + 2 condensation reaction of terephthalaldehyde with either 3,7-dithia-1,9-diaminononane or 1,2-bis(2-aminobenzenethiolate)ethane in place of L^1 used in the present case. The crystal structure analysis of both their copper(I) complexes, $[Cu_2L^4][ClO_4]_2$ and $[Cu_2L^5][ClO_4]_2$, reveal the basic structures are rather similar.[30] Each copper(I) ion is located tetrahedrally in a separate N_2S_2 donor set ‘compartment’. The two bridging phenyl rings are parallel and the dihedral angles between the two rings is *ca.* 80° which leads to a helical arrangement of the molecule.

In the IR spectra of L^2 and L^3 a sharp band observed clearly at 1637 and 1642 cm^{-1} respectively can be attributed to the characteristic C=N stretching vibration. Their ^1H and ^{13}C NMR spectra in particular demonstrated that the compounds are highly symmetrical. In the ^1H-decoupled ^{13}C NMR spectra of L^2 and L^3 nine and eleven characteristic peaks were observed respectively, consistent with the proposed structures; assignments for the spectra are included in the Experimental section. Macrocyclisation was confirmed in the case of the dicopper(I) complex of L^2 by a crystal structure analysis, discussed later. Addition of $[Cu(CH_3CN)_4]ClO_4$ to L^2 and L^3 in acetonitrile yielded yellow air-stable powders $[Cu_2L^2][ClO_4]_2$ and $[Cu_2L^3][ClO_4]_2$ respectively. The former was recrystallised by slow evaporation of the solvent to form X-ray-quality crystals. The recrystallisation of $[Cu_2L^3][ClO_4]_2$ under the same conditions did not yield crystals of suitable quality. The ^1H and ^{13}C NMR spectra of $[Cu_2L^2][ClO_4]_2$ and $[Cu_2L^3][ClO_4]_2$ resemble those of their metal-free macrocycles L^2 and L^3; nine and eleven characteristic peaks were observed in the ^{13}C NMR as for the free macrocycles, consistent with insertion of copper(I) ion in each compartment occurring to produce structurally equivalent compartments. Both $[Cu_2L^2][ClO_4]_2$ and $[Cu_2L^3][ClO_4]_2$ exhibited characteristic C=N stretching vibrations at 1624 and 1643 cm^{-1} respectively, and elemental analysis supported the $[Cu_2L][ClO_4]_2$ formulation with the macrocycles complexed intact.

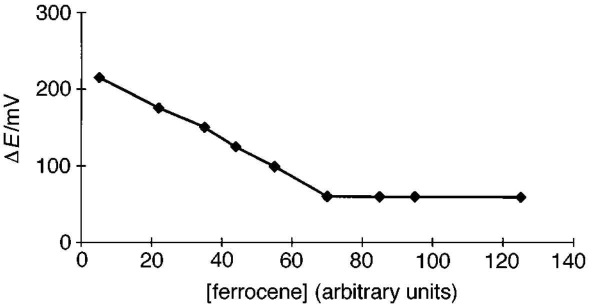


Fig. 1 Effect of ferrocene addition on Δ*E* for the cyclic voltammogram of the Cu^I–Cu^{II} couple in $[Cu_2L^2][ClO_4]_2$ in CH_3CN

The electrochemical properties of the dicopper(I) complexes $[Cu_2L^2][ClO_4]_2$ and $[Cu_2L^3][ClO_4]_2$ have been studied by cyclic voltammetry in acetonitrile and nitromethane in the presence of ferrocene as an internal reference. In acetonitrile the voltammograms of both complexes are similar and show a single quasi-reversible oxidation wave. The oxidation is assigned to the Cu^I–Cu^{II} couple, occurring at $E_{\frac{1}{2}}$ +1.03 and +1.10 V (*vs.* NHE) for $[Cu_2L^2][ClO_4]_2$ and $[Cu_2L^3][ClO_4]_2$ respectively. The Δ*E* values are the same (110 mV), indicating the presence of a reversible, or more properly quasi-reversible, electron process. Corresponding cyclic voltammograms obtained from the analogue $[Cu_2L^4][ClO_4]_2$[30] also show one oxidation wave, $E_{\frac{1}{2}}$ +1.34 V (Δ*E* = 55 mV) (*vs.* NHE). The stabilisation of Cu^I by the tetrahedrally arranged thioether and imine donors in the complexes of L^2 and L^3 compared with L^4 may relate to the slightly larger cavity in the former two ligands and possibly an associated disposition towards flexibility. The change from preferred tetrahedral (Cu^I) to square planar (Cu^{II}) geometry with oxidation and the reverse process for reduction demands flexibility for reversibility to apply.

Somewhat surprisingly, the complexes display enhanced reversibility in voltammetric experiments with addition of increasing amounts of ferrocene. This is possibly associated with ferrocene acting as a ‘bridge’ between the electrode surface and the complex. Surface modification on electrodes to enhance electron-transfer behaviour has been extensively studied for redox proteins,[36,37] but examples of its role with more simple co-ordination compounds are relatively rare. The effect of ferrocene addition on Δ*E* for $[Cu_2L^2][ClO_4]_2$ in CH_3CN is shown in Fig. 1 and the change in the voltammogram is shown in Fig. 2. The Δ*E* values decreased as the concentration of ferrocene increased until Δ*E* *ca.* 60 mV, after which it became constant (Fig. 1). At some stage effective monolayer coverage of the electrode surface is achieved, with Δ*E* then influenced by the electron-transfer rates from the surface to adsorbed

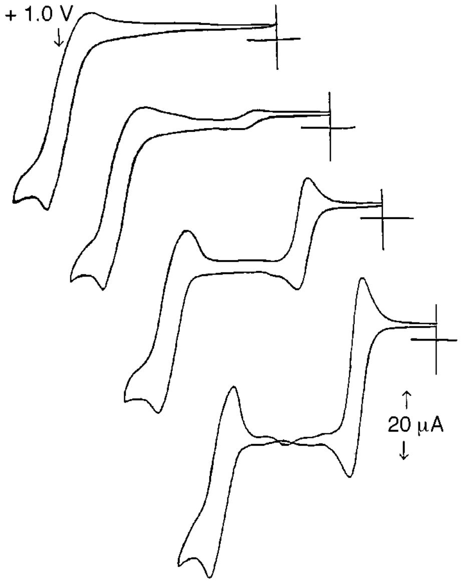


Fig. 2 Variation in the cyclic voltammogram of $[Cu_2L^2][ClO_4]_2$ (left-hand wave) with ferrocene addition (right-hand wave) in CH_3CN (glassy carbon working electrode, range 0.0 to +1.25 V)

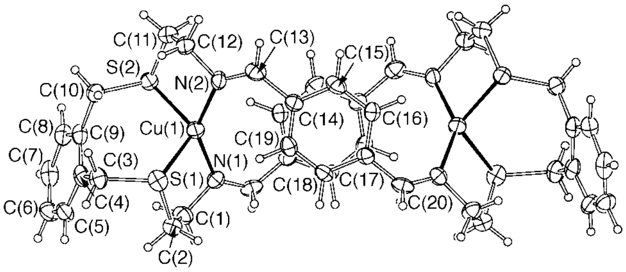


Fig. 3 View of the $[Cu_2L^2]^{2+}$ cation, showing the atom numbering

ferrocene and then to the copper complex; further addition of ferrocene should have no effect, as is observed experimentally.

There is some evidence from structural studies that the solvent acetonitrile potentially may co-ordinate to Cu^I in these systems and cause disruption of the helical structure.[38] Presumably, if acetonitrile does co-ordinate preferentially to Cu^I in solution, an imine–copper(I) bond may be cleaved leading to a different chromophore, and this may result in a Cu^I–Cu^{II} process not typical of a CuN_2S_2 environment.

Therefore the cyclic voltammetric experiments were repeated under the same conditions using the less co-ordinating solvent nitromethane. In nitromethane the voltammograms of both complexes are similar and show a less well defined oxidation process. The oxidations assigned to Cu^I–Cu^{II} for $[Cu_2L^2][ClO_4]_2$ and $[Cu_2L^3][ClO_4]_2$ are observed at potentials of $E_{\frac{1}{2}}$ +1.24 and +1.20 V (*vs.* NHE) respectively. These are similar to those in acetonitrile solvent, but the voltammogram oxidative wave is broad and shows some evidence for two closely following processes with a poorly defined reverse wave. The implication is that the copper(II) species are stabilised in acetonitrile, possibly by weak co-ordination in axial sites, leading to a reversible process. This stabilisation is reduced in the poorly co-ordinating nitromethane, with the process less reversible. The voltammetry experiments do not necessarily comment on the prospect of acetonitrile co-ordination in place of an N- or S-donor in the copper(I) complex. Voltammetric experiments in CH_3NO_2 with addition of increasing amounts of ferrocene also displayed a slightly enhanced reversibility, but less than that in CH_3CN.

The dinuclear complex structure was confirmed in the case of the solvated $[Cu_2L^2][ClO_4]_2$ complex by a crystal structure analysis. An ORTEP[39] drawing of the cation of $[Cu_2L^2]^{2+}$ is shown in Fig. 3, and selected bond lengths and angles for the metal-ion environment are given in Table 1. The structural analysis of $[Cu_2L^2][ClO_4]_2$ reveals that the basic structure is very similar to those of the analogous compounds $[Cu_2L^4][ClO_4]_2$ and $[Cu_2L^5][ClO_4]_2$. The two N_2S_2 donor sets are each tetrahedrally co-ordinated to the copper(I). The two *para*-substituted phenyl rings bridging the two N_2S_2 'compartments' are parallel (separation 3.5 Å), exhibiting π stacking, and a double helical arrangement (figure-of-eight loop) of the ligand backbone is well defined. In terms of the number of aromatic groups incorporated, the ligand L^2 is intermediate between L^4 and L^5. The commonality of structures irrespective of the general ligand framework suggests that the two aromatic rings in the dialdehyde residues are particularly important in defining the helicity.

Table 1 Copper(I) environments (bond distances in Å, angles in °) in $[Cu_2L^2][ClO_4]_2\cdot0.5CH_3OH\cdot2.5H_2O$

Cu(1)–S(1)	2.362(4)	Cu(1)–S(2)	2.337(4)
Cu(1)–N(1)	1.984(9)	Cu(1)–N(2)	1.99(1)
S(1)–Cu(1)–S(2)	113.2(1)	S(1)–Cu(1)–N(1)	88.4(3)
S(1)–Cu(1)–N(2)	111.3(3)	S(2)–Cu(1)–N(1)	115.0(3)
S(2)–Cu(1)–N(2)	88.8(3)	N(1)–Cu(1)–N(2)	140.8(4)

Acknowledgements

Support by the University of Newcastle of D. T. Richens under an academic visitor scheme is gratefully acknowledged.

References

1 E. C. Constable, *Nature* (*London*), 1990, **346**, 314.
2 J.-P. Sauvage, *Acc. Chem. Res.*, 1990, **23**, 319.
3 J.-M. Lehn, *Angew. Chem.*, *Int. Ed. Engl.*, 1990, **29**, 1304.
4 E. C. Constable, *Chem. Ind.* (*London*), 1994, 56.
5 K. D. Karlin and Z. Tyeklar (Editors), *Bioinorganic Chemistry of Copper*, Chapman and Hall, New York, London, 1993.
6 J. Reedijk (Editor), *Bioinorganic Catalysis*, Marcel Dekker, New York, 1993.
7 S. R. Cooper (Editor), *Crown Compounds—Toward Future Applications*, VCH, Weinheim, 1993.
8 P. A. Vigato, S. Tamburini and D. E. Fenton, *Coord. Chem. Rev.*, 1990, **106**, 25.
9 E. I. Solomon, M. J. Baldwin and M. D. Lowery, *Chem. Rev.*, 1992, **92**, 521.
10 T. N. Sorrell, *Tetrahedron*, 1989, **45**, 3.
11 U. Koert, M. M. Harding and J.-M. Lehn, *Nature* (*London*), 1990, **346**, 339.
12 W. Zarges, J. Hall and J.-M. Lehn, *Helv. Chim. Acta*, 1991, **74**, 1843.
13 J. K. Judice, S. J. Keipert and D. J. Cram, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1323.
14 R. Krämer, J.-M. Lehn, A. De Cian and J. Fischer, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 703.
15 E. C. Constable, A. J. Edwards, P. R. Raithby and J. V. Walker, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 1465.
16 A. Bilyk and M. M. Harding, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 77.
17 C. Piguet, G. Bernardinelli, B. Bocquet, A. Quattropani and A. F. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 7440.
18 R. Ziessel and M.-T. Youinou, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 877.
19 D. E. Fenton, R. W. Matthews, M. McPartlin, B. P. Murphy, I. J. Scowen and P. A. Tasker, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1391.
20 T. Adatia, N. Beynek and B. P. Murphy, *Polyhedron*, 1995, **14**, 335.
21 S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461; D. E. Fenton, *Pure Appl. Chem.*, 1986, **58**, 1437.
22 S. R. Cooper, in *Crown Compounds Toward Future Applications*, ed. S. R. Cooper, VCH, Weinheim, 1992, p. 112.
23 R. Menif and A. E. Martell, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1521.
24 D. E. Fenton, S. J. Kitchen, C. M. Spencer, S. Tamburini and R. Vigato, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 685.
25 S. Brooker, V. McKee, W. B. Shepard and L. K. Pannell, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 2555.

26 M. G. B. Drew, D. McDowell and J. Nelson, *Polyhedron*, 1988, **7**, 2229.
27 M. G. B. Drew, D. Marrs, J. Hunter and J. Nelson, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 11.
28 M. P. Ngwenya, A. E. Martell and J. Reibenspies, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1207.
29 G. Morgan, V. McKee and J. Nelson, *Inorg. Chem.*, 1994, **33**, 4427.
30 P. Comba, A. Fath, T. W. Hambley and D. T. Richens, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1883.
31 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985 and 1992.
32 A. Altomare, M. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
33 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, DIRDIF 94, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1994.
34 A. J. Elliott, G. A. Lawrance and G. Wei, *Polyhedron*, 1993, **12**, 851.
35 J. van Rijn and J. Reedijk, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 2579.
36 M. J. Eddowes and H. A. O. Hill, *J. Am. Chem. Soc.*, 1979, **101**, 4461.
37 F. A. Armstrong, H. A. O. Hill and N. J. Walton, *Acc. Chem. Res.*, 1988, **21**, 407.
38 P. Comba, personal communication.
39 C. K. Johnson, ORTEP, A Thermal Ellipsoid Plotting Program, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

Received 13*th August* 1997; *Paper* 7/05932I