Structural, Spectroscopic and Electrochemical Consequences of Displacing the Co-ordinated Thioethers from a Copper(I) N_2S_2 Complex†

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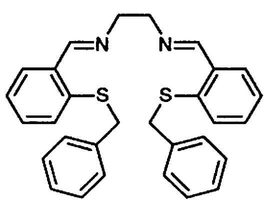
The effect of detaching the two co-ordinated thioethers from the copper(I) N_2S_2 complex *N,N'*-bis{[2-(phenylmethylthio)phenyl]methylene}ethane-1,2-diaminecopper(I) perchlorate, [CuL]ClO_4, has been investigated. This has been achieved by treating this complex with a second mole of the same ligand such that Cu^I becomes co-ordinated to two ligands, each by way of its diimine moiety. The resulting orange coloured complex, [CuL_2]ClO_4, is air-stable in the solid state. Results from X-ray crystal structure analysis indicate that the cation has approximately tetrahedral stereochemistry with a CuN_2–CuN_2 dihedral angle of 90.7(4)°, Cu–N bond lengths all 2.05(1) Å and intrachelate N–Cu–N angles of 83.9(4) and 85.0(4)°. Results from cyclic voltammetry indicate quasi-reversibility of the $Cu^I \longleftrightarrow Cu^{II}$ electron-transfer process, and a standard reduction potential of 0.23 ± 0.02 V *vs.* saturated calomel electrode. Chemical decomposition of the copper(II) species is also apparent, which is consistent with its high reactivity when direct synthesis was attempted.

In previous work[1] we have studied the changes in structure and properties that occur in $[CuL]^+$, where L is the N_2S_2 ligand *N,N'*-bis{[2-(phenylmethylthio)phenyl]methylene}ethane-1,2-diamine, when the copper(I) ion undergoes aerobic oxidation to copper(II), this being a major point of interest in connection with the copper-containing electron-transfer proteins, which have a similar co-ordination environment.[2,3] Of equal interest are the particular attributes of the N_2S_2 donor array, which cause it to be associated with the blue copper proteins. In all of these that have been structurally characterised, two nitrogen donors, arising from histidine residues, and a thiolate sulfur originating from a cysteine residue are present in the primary co-ordination sphere of the copper. In plastocyanin and azurin a thioether sulfur, from a methionine residue, is also present, but at a sufficiently long distance from the copper to render it questionable whether or not it should be considered bonded and whether it has any significant affect on the properties of the molecules. This is especially so as the spectroscopically related protein stellacyanin is totally devoid of methionine.[4] To ascertain the effect of co-ordinating or not co-ordinating a thioether to copper(I) we have now treated $[CuL]^+$ with further ligand, in such a way as to displace the two terminal thioether donors from the copper(I) ion and replace them with a second diimine moiety. As a consequence we can now compare the properties, both in the solid state and in solution, of two very closely related copper(I) complexes, one having an N_2S_2 co-ordinating array and the other an N_4 array, and are able to identify the contributions made to the electronic spectrum and electrochemical behaviour by the pair of co-ordinated thioethers. Earlier comparative work of this type has been undertaken using two sets of ligands, which have differed in that the pair of thioether donors common to one set was replaced by a pair of secondary or tertiary amines in the second set, although in that study none of the copper(I) N_4 complexes was isolated.[5]



L

Experimental

Cyclic voltammetry was conducted in a three-electrode cell having a glassy carbon working electrode, platinum-wire counter electrode and an Ag–$AgNO_3$ reference electrode, using 10^{-3} mol dm^{-3} solutions of the complexes in nitromethane with 10^{-1} mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte. The $E_{\frac{1}{2}}$ values were normalised to the saturated calomel electrode (SCE) *via* the ferrocene–ferrocenium couple. Electronic spectra were recorded using a Hewlett-Packard 8452 diode array spectrophotometer. Instrumentation and methods used for the other physical measurements and for the preparation of L were those described previously.[1]

Preparation.—*Bis*[N,N'-*bis*{[2-(*phenylmethylthio*)*phenyl*]-*methylene*}*ethane*-1,2-*diamine*-N,N',N,N']*copper*(I) *perchlorate* [CuL_2]ClO_4. **CAUTION**: Perchlorate salts of metal complexes are potentially explosive. Although we have had no incidents with this or related compounds suitable precautions should be taken.

A solution of tetrakis(acetonitrile)copper(I) perchlorate (75 mg, 0.23 mmol) in dry deoxygenated ethanol (10 cm^3) was added to a warm solution of L (0.22 g, 0.46 mmol) which had been prepared under argon. The mixture was heated under reflux for 10 min and then allowed to cool slowly to room temperature. After 24 h bright orange crystals of the pure product were collected by filtration under argon, washed with deoxygenated ethanol and dried under vacuum. Yield: 0.15 g (59%); m.p. 116–118 °C (Found: C, 64.0; H, 4.7; N, 5.1. $C_{60}H_{56}ClCuN_4O_4S_4$ requires C, 64.1; H, 5.0; N, 5.0%). ^{13}C

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Crystallographic data for $[CuL_2]ClO_4{\cdot}MeOH$

Empirical formula	$C_{61}H_{60}ClCuN_4O_5S_4$
M	1156.41
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.687(1)
b/Å	18.462(1)
c/Å	13.985(1)
α/°	90.56(1)
β/°	104.42(1)
γ/°	112.74(1)
U/Å^3	2905(1)
λ/Å	0.710 69
D_m/g cm^{-3} [a]	1.32(1)
Z	2
D_c/g cm^{-3}	1.322
$F(000)$	1208
Crystal dimensions/mm	0.05 × 0.15 × 0.28
μ/cm^{-1}	6.29
Transmission coefficients	0.89–0.97
θ_{max}/°	20
h,k,l ranges	$\pm12, \pm13, \pm17$
Scan width/°	$0.55 + 0.35\tan\theta$
Scan mode	ω–θ
No. of reflections sampled	10 834
No. of reflections measured	4602
No used in refinement $[F^2 > 2\sigma(F^2)]$	2683
R_{int}	0.043
No. of parameters refined	675
R [b]	0.069
R'	0.083
Goodness of fit	1.34
Final shift/error (max., av.)	0.49, 0.07

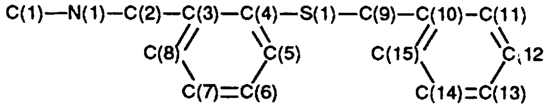
[a] By flotation in a carbon tetrachloride–hexane mixture. [b] $R = \Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma|F_o|^2$.

NMR (CD_3NO_2): δ 161.5 (C=N), 136.5, 136.2, 133.8, 131.0, 130.6, 128.2, 127.9 (8C), 127.3 (8C), 126.5, 125.6 (aromatic C), 60.4 (N–CH_2) and 38.6 (S–CH_2). $\Lambda_M(MeNO_2)$: 86 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte).[6]

Structural Analysis.—Single crystals of $[CuL_2]ClO_4{\cdot}MeOH$ were grown under anaerobic and anhydrous conditions from an acetone solution into which methanol was slowly diffused. The crystal used for data collection was sealed in a thin-walled glass capillary to prevent decomposition through loss of methanol. Unit-cell and intensity data were measured with a CAD-4 diffractometer using graphite-monochromated Mo-Kα X-radiation. Unit cell parameters (Table 1) were determined from a least-squares fit to the setting angles of 25 reflections chosen widely in reciprocal space each at four different values of ψ in the θ range 8–12°. The space group was determined from precession photographs with $P\bar{1}$ ultimately chosen on the basis of the structure solution and refinement. Three reflections monitored every 120 min of exposure time showed no significant variation in intensity. Absorption corrections were applied (Gaussian quadrature, 8 × 8 × 8 grid). The crystals were of poor quality and weakly diffracting, 4602 of the 10 834 reflections sampled had $\sigma(I)/I < 1.33$ on the fast scan and were not remeasured. The unit cell used for data collection had the dimensions: $a = 12.687(1)$, $b = 13.985(1)$, $c = 17.909(1)$ Å, $\alpha = 79.25(1)$, $\beta = 71.94(1)$, $\gamma = 75.58(1)$°. This cell is related to the reduced cell used in the structure solution and subsequent calculations by the matrix: 1,0,0; −1,0,1; 0,−1,0.

The crystal structure was solved by Patterson and Fourier methods. Hydrogen atoms were placed in calculated positions with arbitrarily assigned isotropic thermal parameters. The methanol molecule hydrogen atoms were not included. Non-hydrogen atomic coordinates and, with the exception of those for C(13A) and C(14A), anisotropic thermal parameters were refined by full-matrix least squares minimising $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Values of $\sigma^2(F_o^2)$ were obtained from a combination of counting statistics and mean deviations. Hydrogen-atom coordinates and thermal parameters were not refined.

Computer programs of the XTAL system[7] were used in the structure determination and refinement. The program CRYLSQ[8] was used for least-squares refinement with neutral atom scattering factors for all atoms. A refinement summary is given in Table 1. The final positional coordinates for the complex are given in Table 2. Ligands are labelled A or B and one half of each is primed or not primed, with the following numbering sequence.



The position of the phenyl group, C(10A)–C(15A), was not well defined. Atoms C(13A) and C(14A) were assigned isotropic thermal parameters because anisotropic ones refined to physically impossible values. Maximum and minimum values in the final difference map were +0.45 and −0.46 e Å^{-3}.

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

Results and Discussion

Co-ordination of a single molecule of L to a copper(I) ion affords a situation in which the ligand locks on to the metal ion by way of the inner, strongly chelating, diimine moiety and additionally by way of the two terminal thioether donors, producing a distorted tetrahedral complex [CuN_2–CuS_2 dihedral angle = 60.0(1)°].[1] Thioether donors are notoriously labile, however,[9] and being at the termini of the quadridentate L are susceptible to displacement by more effective electron-pair donors without the entire ligand necessarily being displaced from the metal. We found that by treating an ethanolic solution of the orange $[CuL]ClO_4$ with a second molecule of ligand, per copper(I) ion, it is possible to produce a lighter orange, slightly more air-sensitive, complex which analysed as $[CuL_2]ClO_4$. Carbon-13 NMR spectra in CD_3NO_2 indicated that both ligand molecules are equivalently bound and this, together with an upfield shift of 5.6 ppm for the S–CH_2 resonance, relative to its chemical shift in $[CuL]ClO_4$, among other smaller changes in resonance positions, supported the possibility of tetrahedral co-ordination at Cu^I, *via* the two diimine moieties, with the thioethers detached.

This structural assignment was confirmed by X-ray crystallography.

Crystal and Molecular Structure of $[CuL_2]ClO_4{\cdot}MeOH$.—Recrystallization of $[CuL_2]ClO_4$ by vapour diffusion of methanol into an acetone solution gave single crystals of $[CuL_2]ClO_4{\cdot}MeOH$. These were suitable for X-ray diffraction work providing that they were retained in an environment saturated with methanol, as desolvation occurs rapidly on exposure to air causing the crystals to crumble. X-Ray analysis indicated regular tetrahedral co-ordination of the two diimine moieties around Cu^I (Fig. 1) with the CuN(1A)N(1A′)–CuN(1B)N(1B′) dihedral angle being 90.7(4)°. The Cu–N bond lengths are all 2.05(1) Å, identical to the average found in $[CuL]ClO_4$, and the intrachelate ring N–Cu–N angles of 83.9(4) and 85.0(4)° are similar to the 82.7(1)° angle found in $[CuL]ClO_4$.[1] The methanol molecule appears to be loosely held in the structure by a hydrogen bond between the hydroxy group and a perchlorate oxygen [O···O 3.04(2) Å, C–O···O 91(1)°]. Other bond lengths and bond angles are unremarkable.

Electrochemical and Spectral Properties.—Cyclic voltam-

Table 2 Atomic positional parameters for $[CuL]ClO_4$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Cu	0.469 5(1)	0.231 14(8)	0.287 3(1)
S(1A)	0.522 3(3)	0.100 1(2)	0.586 1(3)
S(1B)	0.173 3(3)	−0.065 3(2)	0.087 0(3)
S(1A′)	0.249 6(3)	0.400 5(2)	0.055 4(2)
S(1B′)	0.915 2(3)	0.449 8(2)	0.321 3(3)
N(1A)	0.508 7(8)	0.280 8(5)	0.430 0(6)
N(1B)	0.460 7(9)	0.119 3(5)	0.259 6(6)
N(1A′)	0.328 1(7)	0.262 2(4)	0.264 3(7)
N(1B′)	0.597 6(8)	0.265 0(6)	0.212 9(6)
C(1A)	0.431(1)	0.321 4(6)	0.434 6(7)
C(1A′)	0.311 5(9)	0.278 4(6)	0.361 1(9)
C(1B)	0.574(1)	0.129 5(7)	0.240(1)
C(1B′)	0.602 6(9)	0.192 7(8)	0.171 2(9)
C(2A)	0.571(1)	0.271 3(6)	0.509 6(9)
C(2A′)	0.266 6(8)	0.279 2(6)	0.186(1)
C(2B)	0.379(1)	0.049 5(7)	0.241 6(8)
C(2B′)	0.679(1)	0.331 0(9)	0.209 2(8)
C(3A)	0.657(1)	0.234 2(9)	0.512 3(8)
C(3A′)	0.274 2(9)	0.263 6(8)	0.086 3(9)
C(3B)	0.263(1)	0.026 8(7)	0.262(1)
C(3B′)	0.681(1)	0.407 6(8)	0.241 9(8)
C(8A)	0.753(2)	0.276 2(7)	0.477 4(9)
C(8A′)	0.285 2(9)	0.194 3(8)	0.059(1)
C(8B)	0.262(1)	0.059 3(7)	0.351(1)
C(8B′)	0.575(1)	0.418 9(7)	0.216 3(8)
C(7A)	0.840(1)	0.248(1)	0.474(1)
C(7A′)	0.290(1)	0.178 2(8)	−0.036(1)
C(7B)	0.158(2)	0.033 5(8)	0.378 9(9)
C(7B′)	0.574(1)	0.492 5(9)	0.241(1)
C(6A)	0.824(2)	0.175(1)	0.504(1)
C(6A′)	0.280(1)	0.230(1)	−0.105(1)
C(6B)	0.055(1)	−0.026 0(9)	0.320(1)
C(6B′)	0.680(1)	0.553 2(7)	0.291 4(9)
C(5A)	0.730(2)	0.131 2(8)	0.540(1)
C(5A′)	0.268(1)	0.297 0(8)	−0.078(1)
C(5B)	0.058(1)	−0.056 4(7)	0.229(1)
C(5B′)	0.784(1)	0.542 2(7)	0.314 3(8)
C(4A)	0.646(1)	0.161 8(9)	0.545 1(9)
C(4A′)	0.263 5(9)	0.314 2(7)	0.017(1)
C(4B)	0.161(1)	−0.031 9(7)	0.198 5(9)
C(4B′)	0.788(1)	0.469 3(8)	0.290 1(8)
C(9A)	0.525(2)	0.159 5(9)	0.689(1)
C(9A′)	0.266(1)	0.460 4(7)	−0.043 1(9)
C(9B)	0.023 8(9)	−0.129 4(6)	0.021 8(9)
C(9B′)	1.035(1)	0.545 1(6)	0.351 0(9)
C(10A)	0.463(2)	0.108(1)	0.760(2)
C(10A′)	0.268(2)	0.537 9(9)	−0.010(1)
C(10B)	0.023(1)	−0.162 8(9)	−0.077(1)
C(10B′)	1.149(1)	0.534 9(7)	0.357(1)
C(11A)	0.512(2)	0.098(1)	0.855(2)
C(11A′)	0.373(1)	0.602(1)	0.030(1)
C(11B)	0.044(1)	−0.230(1)	−0.082(1)
C(11B′)	1.207(2)	0.558 0(9)	0.284(1)
C(12A)	0.428(3)	0.045(1)	0.905(1)
C(12A′)	0.370(1)	0.672(1)	0.063(1)
C(12B)	0.040(1)	−0.264 2(9)	−0.172(2)
C(12B′)	1.309(2)	0.548(1)	0.292(1)
C(13A)	0.314(2)	0.012(1)	0.850(2)
C(13A′)	0.263(2)	0.678 8(9)	0.050(1)
C(13B)	0.014(1)	−0.232(1)	−0.256(1)
C(13B′)	1.353(1)	0.513(1)	0.365(1)
C(14A)	0.275(2)	0.019(1)	0.765(2)
C(14A′)	0.161(1)	0.616(1)	0.009(1)
C(14B)	−0.005(1)	−0.166(1)	−0.253(1)
C(14B′)	1.298(1)	0.489 2(8)	0.439(1)
C(15A)	0.346(2)	0.068(1)	0.716(1)
C(15A′)	0.160(1)	0.545 3(9)	−0.023(1)
C(15B)	−0.001(1)	−0.130 6(7)	−0.165(2)
C(15B′)	1.195(1)	0.500 4(8)	0.433(1)
Cl	0.174 8(4)	0.227 9(3)	0.587 4(3)
O(1)	0.127 9(8)	0.232 2(5)	0.666 2(6)
O(2)	0.158 0(9)	0.283 2(6)	0.525 3(7)
O(3)	0.296(1)	0.248 7(7)	0.622 6(9)
O(4)	0.116(1)	0.155 0(6)	0.532 9(8)
C(16)	1.109(1)	0.744 3(9)	0.235(1)
O(16)	0.996(1)	0.704 3(7)	0.216(1)

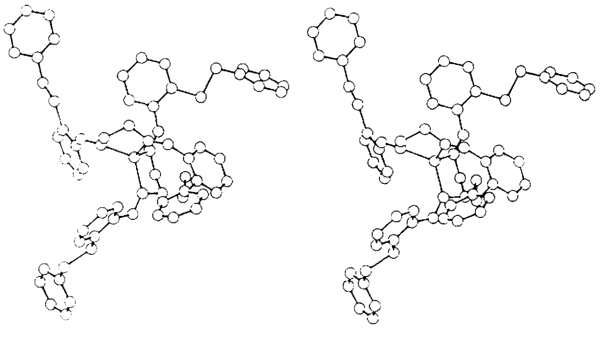


Fig. 1 Stereoview of the non-hydrogen atoms of the complex cation $[CuL_2]^+$

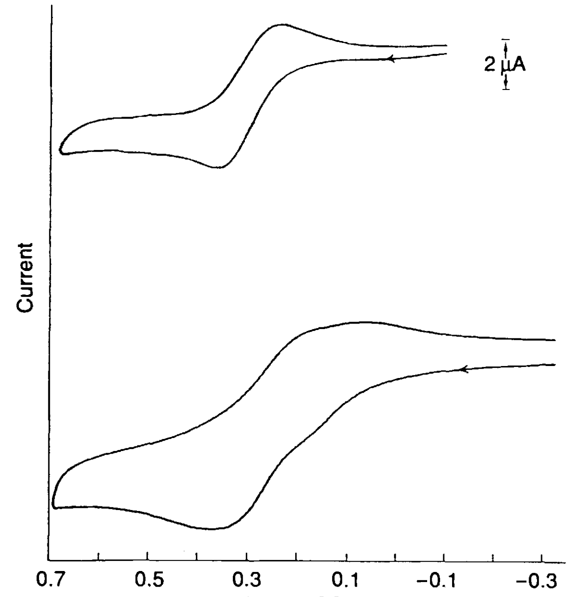


Fig. 2 Cyclic voltammograms for $[CuL]^+$, at 10 mV s^{-1} (upper trace) and $[CuL_2]^+$, at 50 mV s^{-1} (lower trace)

mograms for $[CuL]^+$ and $[CuL_2]^+$ in $MeNO_2$ are shown in Fig. 2. Nitromethane was chosen as solvent because of the low probability of it associating with the complexes.[10] Both complexes show quasi-reversible electrochemical behaviour with peak-to-peak separations well in excess of 58 mV even at scan rates as low as 10 mV s^{-1}. The cation $[CuL_2]^+$ shows the added complication of chemical irreversibility which causes poorly defined anodic and cathodic peaks at the slower scan rates. Increasing the scan rate to 50 mV s^{-1} produced better resolved peaks and enabled an $E_{\frac{1}{2}}$ value of 0.23 ± 0.02 V *vs.* SCE to be determined, but it should be noted that the peak separation at this scan rate is *ca.* 300 mV and thus the accuracy of this $E_{\frac{1}{2}}$ determination is questionable.[11] The error of ±0.02 V given here refers only to the imprecision associated with locating the position of maximum current in the rather broad cathodic wave. The scan rate of 50 mV s^{-1} used for the

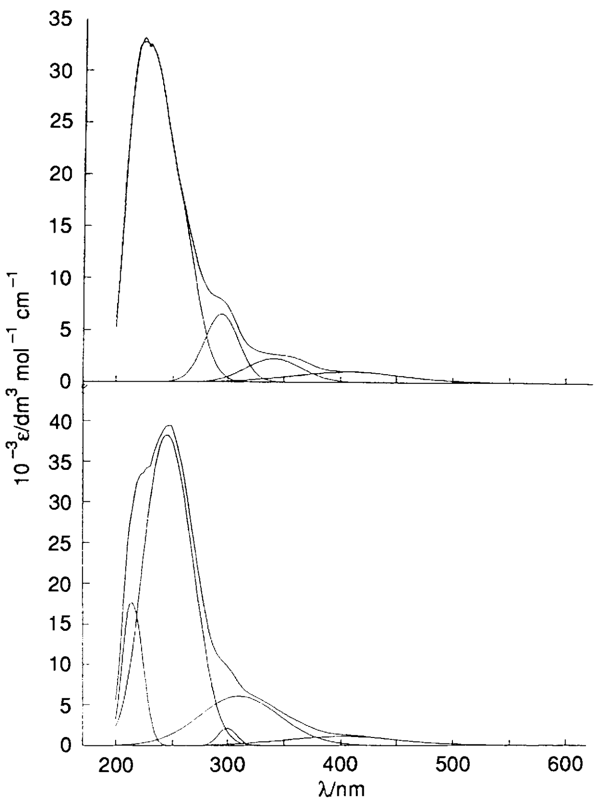
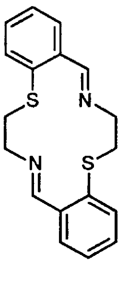


Fig. 3 Electronic spectra and the Gaussian resolution thereof for $[CuL]^+$ (top) and $[CuL_2]^+$ (bottom), recorded in deoxygenated EtOH, $c = 7.5 \times 10^{-5}$ mol dm^{-3}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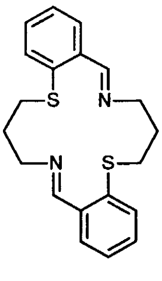
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determination of $E_{\frac{1}{2}}$ represents a compromise between the deleterious affects of the quasi-reversible electrochemical behaviour, which favours a measurement at slow scan rate, and the tendency towards chemical irreversibility, which necessitates a measurement at high scan rate. Increasing the scan rate to 300 mV s^{-1} increased the inter-peak separation to *ca.* 620 mV. Experimentation with other solvents and with a platinum electrode rather than a glassy carbon electrode failed to produce more useful results. The $E_{\frac{1}{2}}$ value of 0.23 V should be compared with the value of 0.29 V obtained for $[CuL]^+$ (ref. 1) as it indicates that detachment of the thioethers does not cause a major shift in the standard reduction potential of the system.

The chemical irreversibility shown by $[CuL_2]^+$ in the cyclic voltammetry experiment may be associated with molecular rearrangement or decomposition initiated by the oxidative process. This would be consistent with the broad cathodic peak, which appears to include two partially superimposed waves, and with our repeated failure to isolate $[CuL_2]^{2+}$, under either hydrous or anhydrous conditions. Under hydrous conditions $\{[Cu(H_2O)_6][ClO_4]_2$ plus 2 equivalents of L in EtOH$\}$ it is apparent that hydrolysis of the imines occurs, as quantities of 2-(phenylmethylthio)benzaldehyde and the 1,2-diaminoethane adduct of copper(II) were collected. Under anhydrous conditions $\{[Cu(Me_2SO)_4][ClO_4]_2$ plus 2 equivalents of L in EtOH$\}$ no tractable product could be formed. This stands in contrast to the ease with which we were able to isolate and characterise $[CuL(H_2O)][ClO_4]_2$.[1]

The electronic spectral changes that accompany the displacement of the thioethers may be seen in Fig. 3. The principal change is the shift of the dominant, intraligand, $\pi \longrightarrow \pi^*$ transition to longer wavelength [from λ/nm 222 (ε/dm^3 mol^{-1} cm^{-1} 33 000) to 244 (38 000) and 214 (18 000) (sh)] as might be expected on the grounds that the diminished participation of the electron density of sulfur in the conjugated π system is restored upon detachment. Superimposed on the low-energy tail of the major band, in each case, are three shoulders or areas of enhanced absorption, whose position and intensity have been clarified, in Fig. 3, by Gaussian resolution. The highest energy shoulder {λ/nm 294 (ε/dm^3 mol^{-1} cm^{-1} 6600) in $[CuL]^+$ and 300 (2100) in $[CuL_2]^+$} in each case is almost certainly the $n \longrightarrow \pi^*$ transition associated with the imine groups, as this occurs at 320 nm (ε 3000 dm^3 mol^{-1} cm^{-1}) in free L and would be expected at higher energy in the complexes.[12] The other two shoulders {λ/nm 341 (ε/dm^3 mol^{-1} cm^{-1} 2300) and 407 (990) in $[CuL]^+$, 310 (6100) and 401 (1100) in $[CuL_2]^+$} are absent in the spectrum of free L and appear to be metal–ligand charge transfer (m.l.c.t.) bands. Our reason for suggesting this stems from the similar, but better resolved spectra shown by the closely related macrocyclic complexes $[CuL']^+$ and $[CuL'']^+$, which we have studied previously[13] {$[CuL']^+$ λ/nm 216 (ε/dm^3 mol^{-1} cm^{-1} 58 000), 299 (8900), 356 (2300) and 480 (750); $[CuL'']^+$; 211 (46 000), 301 (8300), 344 (3800) and 474 (1900)} and their $E_{\frac{1}{2}}$ values, measurable by cyclic voltammetry in methanol, which we found to be 0.23 and 0.47 V, respectively, *vs.* SCE. In these complexes both the low-energy shoulders occur at higher energies and with greater intensities in the spectrum of the more weakly reducing complex, characteristics generally associated with m.l.c.t. bands.[5] For $[CuL]^+$ and $[CuL_2]^+$, the corresponding shoulders have higher energies and intensities in the spectrum of $[CuL_2]^+$ indicating, if the same reasoning is applied, that it has a standard reduction potential in excess of 0.29 V *vs.* SCE, however it is not possible to quantify this. Taken with the $E_{\frac{1}{2}}$ value determined from the cyclic voltammetry we conclude that the standard reduction potential for $[CuL_2]^+$ is not greatly different from that shown by $[CuL]^+$. Although this may be contrary to expectations, on the grounds that thioether donors tend to favour higher reduction potentials for the Cu^{II}–Cu^{I} couple over those produced by nitrogen donors,[14,15] it may be the case here that the much more regular tetrahedral stereochemistry of the N_4 complex compensates for the loss of the thioethers, such that the reduction potential remains largely unchanged.

Conclusion

This analysis demonstrates that there is no dramatic change to the electronic structure of $[CuL]^+$ when the pair of chelating thioethers is replaced by a second, bidentate, non-conjugated diimine and, when associated with this, there is a concomitant change from a highly distorted tetrahedral structure to a regular tetrahedral one. What does become evident, however, is that the chemical reversibility of the $Cu^{I} \longleftrightarrow Cu^{II}$ electron transfer is, to some extent, lost. This appears to be associated with enhanced reactivity of the copper(II) bound imines, which develops upon detachment of the thioethers, and implies that the co-ordinated thioethers perform a significant protecting role in the more stable complex $[CuL(H_2O)][ClO_4]_2$.

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