Copper(II) Complexes of Tetradentate Schiff-base Ligands derived from Aminothioetherimidazoles. Crystal Structure Determination of {*N*-2-[(5'-Methylimidazol-4'-yl)methylthio]ethylsalicylideneiminato(1−)-*O,N,N',S*}-copper(II) Perchlorate†

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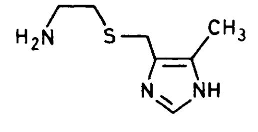
Copper(II) complexes of tetradentate Schiff bases derived from aminothioetherimidazoles are described. The crystal structure of the cationic copper(II) complex of the Schiff base derived from the condensation of 4-[(2-aminoethyl)thiomethyl]-5-methylimidazole and salicylaldehyde, $[Cu(HL^1)][ClO_4]$, has been determined by *X*-ray diffraction methods. Crystals are monoclinic, with $a = 10.32(3)$, $b = 11.41(3)$, $c = 14.34(4)$ Å, $\beta = 89.33(5)°$, space group $P2_1/c$; 1 196 reflections with $I/\sigma(I) > 3.0$ gave $R = 0.0587$. The copper is in a tetrahedrally distorted, square-planar environment; the imidazole NH is hydrogen bonded to the perchlorate anion.

The active sites of copper proteins, for which *X*-ray crystal structures are available, contain copper(II) bound by two, or more, histidine imidazole groups.[1] Consequently it is of interest to prepare complexes of ligands containing azole groups as small molecule models for copper(II) biosites.[2,3] Imidazole-containing Schiff-base ligands can act as versatile models for copper protein environments.[4] Not only do they give opportunity to study Type 1 copper sites, in which a distorted metal ion environment of low symmetry is present, [5] but also Type 2 copper sites such as that present in bovine erythrocyte superoxide dismutase where an imidazolate bridges the heterobinuclear copper–zinc pair[6] (Figure 1).

In this paper we report the synthesis of copper(II) complexes of tetradentate Schiff bases derived from aminothioether-imidazoles and the crystal structure of the cationic copper(II) complex of the Schiff base derived from the condensation of 4-[(2-aminoethyl)thiomethyl]-5-methylimidazole (Hatmi) and salicylaldehyde (Hsal), $[Cu(HL^1)]ClO_4$.

Results and Discussion

Cationic Complexes of Schiff Bases derived from Hatmi.—The compound 4-[(2-aminoethyl)thiomethyl]-5-methylimidazole (Hatmi), an intermediate in the production of the anti-ulcer drug cimetidine,[7] is a particularly attractive candidate as a precursor to tetradentate Schiff bases as it contains both imidazole and thioether functions. Treatment of an ethanolic solution of Hatmi with an equimolar amount of salicylaldehyde (Hsal) gave a bright yellow solution of the Schiff base H_2L^1. Addition of equimolar amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ and methanolic NaOH to this solution yielded the brown-green complex $[Cu(HL^1)]ClO_4$. The complex $[Cu(HL^2)]ClO_4 \cdot 0.5H_2O$ was recovered as a light brown solid from the corresponding reaction starting from 5-bromosalicylaldehyde.



Hatmi

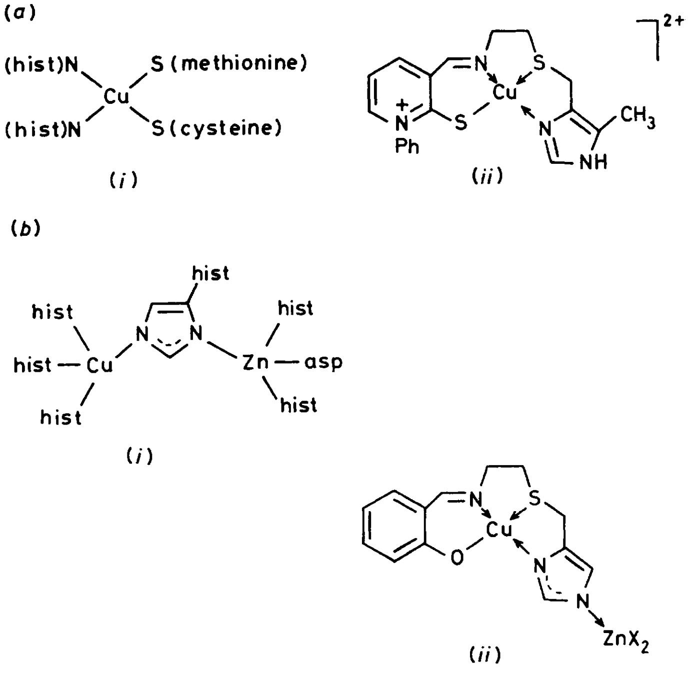
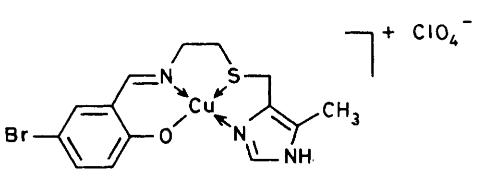


Figure 1. A comparison of the metal environments in (*a*) plastocyanin (*i*) (ref. 5) and a 'model' complex (*ii*) (ref. 9); (*b*) superoxide dismutase (*i*) (ref. 6) and a 'model' complex (*ii*) (ref. 15)



$[Cu(HL^2)]ClO_4$

The i.r. spectra of the complexes each show a broadened band near 3 300 cm^{-1} indicative of the stretching vibration of the imidazole NH group. The absence of a phenolic ν(OH) indicates preferential deprotonation of the phenol on addition of one equivalent of NaOH. A strong band between 1 620 and 1 630 cm^{-1} is consistent with imine formation. The ν_3(ClO) and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

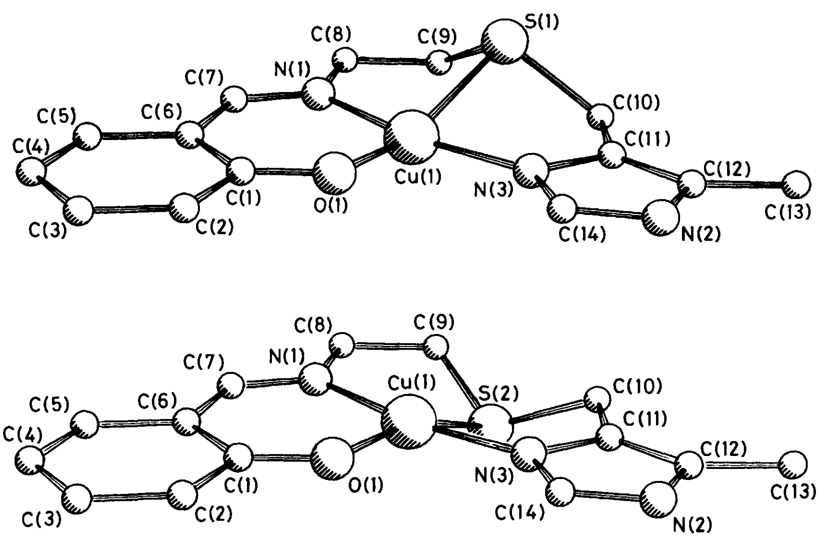


Figure 2. The structures of the two conformations of the cation $[\mathrm{Cu(HL^1)}]^+$ with atom labelling

ν_4(ClO) vibrations of the anion, in both complexes, are split into three and two bands respectively indicating a C_{2v} environment for the perchlorate anion.[8] At first it was thought that the anion was interacting with the metal but a subsequent *X*-ray structure revealed that one of the O atoms of the anion is hydrogen bonded to the NH group of the imidazole ring. This also helps explain the broad nature of the imidazole NH stretch.

The optical spectra of the complexes were recorded in the solid state (by diffuse reflectance) and in dimethyl sulphoxide (dmso) solution. The complex $[\mathrm{Cu(HL^1)}]\mathrm{ClO_4}$ shows a broad absorption at 581 nm, with a discernible shoulder at 667 nm, in the solid state; in dmso a band is found at 635 nm (ε 193 dm^3 mol^{-1} cm^{-1}). Casella[9] has reported that the spectrum recorded in $\mathrm{CH_3CN}$ shows an absorption at 584 nm closely similar to the solid-state result and suggesting a retention of the structure in solution; it is therefore likely that the large red shift noted in dmso is a function of the speciation in that solvent. Similarly $[\mathrm{Cu(HL^2)}]\mathrm{ClO_4}$ exhibits a broad absorption at 574 nm in the solid which moves to 634 nm (ε 214 dm^3 mol^{-1} cm^{-1}) in dmso. There appears to be little influence of the Br substituent on the spectrum, thus parallelling recent observations by Atkins *et al.*[10] on a series of salicylaldehyde-based copper(II) Schiff-base complexes. The *d–d* transitions of both complexes are quite intense suggesting that the geometry at the metal ion could be distorted from square planar or tetragonal.[11] The diffuse reflectance spectra were also recorded in the near-u.v. region and both spectra showed intense, broad, poorly resolved bands between 300 and 400 nm, with a less intense shoulder at *ca.* 450 nm. This may be assigned to an O(phenolate) $\longrightarrow$ Cu$^{\rm II}$ ligand-to-metal charge-transfer band[12] or to a Cu$^{\rm II}$ $\longrightarrow$ π*(phenolate) metal-to-ligand charge-transfer band;[13] the bands in the higher energy region may be associated with imidazole(π) $\longrightarrow$ Cu$^{\rm II}$ and thioether S(σ) $\longrightarrow$ Cu$^{\rm II}$ ligand-to-ligand charge transfers.[13,14] The poor resolution in this region precludes accurate assignments.

The *X*-ray crystal structure of $[\mathrm{Cu(HL^1)}]\mathrm{ClO_4}$ shows that the complex consists of a molecular $[\mathrm{Cu(HL^1)}]^+$ cation which is hydrogen bonded to the $\mathrm{ClO_4}^-$ anion. In the solid state the individual cations possess no imposed symmetry and are therefore chiral: however, the crystal consists of a racemic mixture in the centrosymmetric space group $P2_1/c$. In addition, each cation site in the lattice shows a 50:50 disorder of the sulphur atom, producing two conformers which are enantiomeric at the sulphur. The structures of these two conformers are shown in Figure 2 and selected bond lengths and angles are given in Table 1.

Table 1. Selected bond lengths (Å) and angles (°) with estimated standard deviations, and non-bonded contacts (Å) for $[\mathrm{Cu(HL^1)}]\mathrm{ClO_4}$*

Cu(1)–S(1)	2.428(6)	C(11)–C(12)	1.352(16)
Cu(1)–S(2)	2.409(6)	C(12)–C(13)	1.507(17)
Cu(1)–O(1)	1.873(8)	N(2)–C(12)	1.369(15)
Cu(1)–N(1)	1.890(9)	N(2)–C(14)	1.324(14)
Cu(1)–N(3)	1.927(9)	N(3)–C(14)	1.321(14)
N(1)–C(7)	1.272(14)	N(3)–C(11)	1.398(14)
N(1)–C(8)	1.479(15)	Cu(1) ··· Cu(1$^{\rm I}$)	3.797(8)
S(1)–C(9)	1.600(18)	Cu(1) ··· O(4$^{\rm II}$)	3.437(18)
S(2)–C(9)	1.596(18)	S(1) ··· O(1$^{\rm I}$)	2.967(10)
S(1)–C(10)	1.834(13)	S(2) ··· O(5$^{\rm II}$)	3.107(18)
S(2)–C(10)	1.816(13)	O(2) ··· N(2)	2.850(21)
		O(2) ··· H[N(2)]	1.91
S(1)–Cu(1)–O(1)	156.8(3)	C(7)–N(1)–C(8)	118.3(9)
S(1)–Cu(1)–N(1)	83.7(3)	Cu(1)–S(1)–C(9)	88.7(7)
S(1)–Cu(1)–N(3)	84.1(3)	Cu(1)–S(1)–C(10)	91.5(4)
S(2)–Cu(1)–O(1)	161.8(3)	C(9)–S(1)–C(10)	114.0(8)
S(2)–Cu(1)–N(1)	84.1(3)	Cu(1)–S(2)–C(9)	89.5(7)
S(2)–Cu(1)–N(3)	85.4(3)	Cu(1)–S(2)–C(10)	92.5(5)
O(1)–Cu(1)–N(1)	97.2(4)	C(9)–S(2)–C(10)	115.2(8)
O(1)–Cu(1)–N(3)	94.9(4)	C(12)–N(2)–C(14)	109.1(9)
N(1)–Cu(1)–N(3)	167.6(4)	Cu(1)–N(3)–C(11)	118.6(7)
Cu(1)–O(1)–C(1)	124.8(7)	Cu(1)–N(3)–C(14)	135.7(8)
Cu(1)–N(1)–C(7)	123.3(8)	C(11)–N(3)–C(14)	105.7(9)
Cu(1)–N(1)–C(8)	118.3(7)		

* Symmetry operations: I, $-x$, $-y$, $-z$; II, x, $-0.5 - y$, $-0.5 + z$.

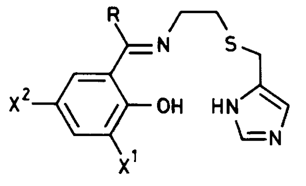
The copper(II) in the cation is four-co-ordinate, bound by the deprotonated phenolic oxygen, imine, and imidazole-type nitrogens, and the thioether sulphur atoms. The Cu–O and Cu–N lengths are in the range found for similar Cu–O(phenolate), Cu–N(imine), and Cu–N(imidazole) interactions and the average Cu–S distance of 2.42 Å, although not as long as that found for the Cu–S(thioether) bonds in Type 1 copper proteins,[5] is comparable with those found in Reedijk's '$\mathrm{N_2S_2}$' model complexes.[2,3] The benzene and imidazole rings and the six-membered chelate ring are almost coplanar: the benzene and chelate rings are tilted with respect to each other by 0.5°, and with respect to the imidazole ring plane by 2.8 and 2.5°

respectively. The oxygen and two nitrogen donor atoms and the central copper(II) ion can therefore be considered to lie in an approximate plane from which the sulphur atom is displaced, to one side or the other, by a mean distance of 0.85 Å, leading to N(1)–C(8)–C(9)–S torsion angles of −37.2 or +39.0°. The short C(9)–S bonds (1.6 Å), together with the large vibrational amplitude of atom C(9) parallel to the *c* axis clearly show that atom C(9) is also disordered over two closely adjacent sites which, when used, would serve to increase the magnitudes of these torsion angles as well as the bond lengths.

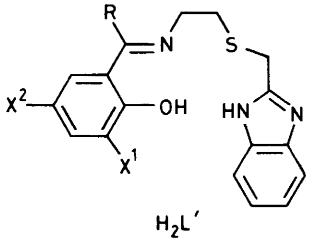
This large out-of-plane displacement of the sulphur constitutes a movement from square planar towards tetrahedral geometry around the copper. The co-ordination of the metal ion in this unusual environment has necessitated enlarged angles: C(6)–C(1)–O(1) to 124.7(10)° and Cu(1)–N(3)–C(14) to 135.7(8)°. Atom O(2) from the anion is hydrogen bonded to the imidazole moiety at an O ··· H(N) distance of 1.91 Å (O ··· N 2.85 Å). The copper atom carries no axial ligands, but both sites are remotely occupied, one by a centrosymmetrically related copper atom at 3.80 Å, and the other by a *c*-glide related perchlorate oxygen O(4) at 3.44 Å. Both the sulphur sites make rather short contacts to oxygen atoms [S(1) ··· O(1) ($-x$, $-y$, $-z$) 2.97; S(2) ··· O(5) (x, $-0.5-y$, $-0.5+z$) 3.11 Å], neither of which shows any sign of disorder. The first of these distances in particular, is much less than the sum of the van der Waals radii, but neither atom carries a hydrogen so hydrogen bonding can be discounted, and since there is no dimerisation across the inversion centre, the interaction cannot be viewed as an inevitable consequence. Neither is there a satisfactory crystallographic explanation for this apparently short distance. A reduction of the space group symmetry to *Pc*, thereby making only approximate the inversion symmetry between the two molecules exhibiting this short contact, would lead to very evident disorder (at least in terms of thermal vibrations) if an attempt were made to refine the structure in $P2_1/c$. However, with the exception of the sulphur atom and, to a lesser extent C(9), there is no sign of disorder in the molecular structure. The crystal was clearly not twinned, although the value of β [89.33(5)°] might have encouraged it. In order to avoid this short 2.97 Å interaction, atom S(2) would be the only permissible sulphur site, although it too shows a rather short 3.11 Å interaction to a *c*-glide related perchlorate oxygen.

Consideration of the structure of the $[Cu(HL^1)]^+$ cation reveals that the co-ordination geometry at the metal ion is not unlike that found in the Type 2 centre present in bovine erythrocyte superoxide dismutase.[6] Furthermore the pyrrolic imidazole proton is ideally sited for further metal complexation, upon deprotonation, to give homo- or hetero-binuclear complexes with an imidazolate bridge.

At this point in this project Casella[9] published his work on the derivation of N_2SS' sites from Hatmi and 3-formyl-1-phenyl-2-(1*H*)-pyridinethione, including the preparation of $[Cu(HL^1)]ClO_4$. This and the suspicion that the presence of a methyl group, in the position adjacent to the nitrogen in the imidazole ring to be used for further complexation, would inhibit the complexation on steric grounds[15] led to our concentrating on examining complexes derived from the related amines 4(5)-[(2-aminoethyl)thiomethyl]imidazole (Hati) and 2-[(2-aminoethyl)thiomethyl]benzimidazole (Hatb). In the latter case it was felt that the change in position of substitution on the imidazole ring and the presence of the fused benzene ring, although not expedient for the preparation of binuclear imidazole-bridged complexes, might confer interesting steric properties on the complexes.

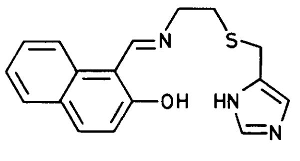


H_2L

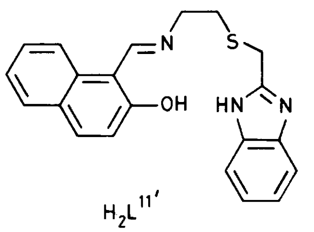


H_2L'

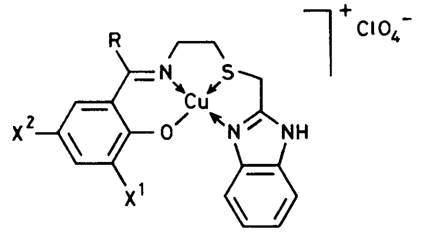
	R	X^1	X^2	
H_2L^3	H	H	H	$H_2L^{3'}$
H_2L^4	H	H	Br	$H_2L^{4'}$
H_2L^5	H	NO_2	H	$H_2L^{5'}$
H_2L^6	H	H	NO_2	$H_2L^{6'}$
H_2L^7	H	H	Cl	$H_2L^{7'}$
H_2L^8	H	Cl	Cl	$H_2L^{8'}$
H_2L^9	CH_3	H	H	$H_2L^{9'}$
H_2L^{10}	CH_3	H	CH_3	$H_2L^{10'}$



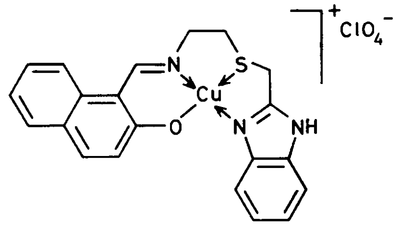
H_2L^{11}



$H_2L^{11'}$



	R	X^1	X^2
$[Cu(HL^{3'})]ClO_4$	H	H	H
$[Cu(HL^{4'})]ClO_4$	H	H	Br
$[Cu(HL^{5'})]ClO_4$	H	NO_2	H
$[Cu(HL^{6'})]ClO_4{\cdot}H_2O$	H	H	NO_2
$[Cu(HL^{7'})]ClO_4{\cdot}0.5EtOH$	H	H	Cl
$[Cu(HL^{8'})]ClO_4$	H	Cl	Cl
$[Cu(HL^{9'})]ClO_4{\cdot}0.5H_2O$	CH_3	H	H
$[Cu(HL^{10'})]ClO_4{\cdot}0.5H_2O$	CH_3	H	CH_3

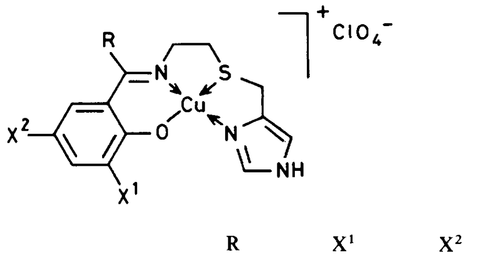


$[Cu(HL^{11'})]ClO_4$

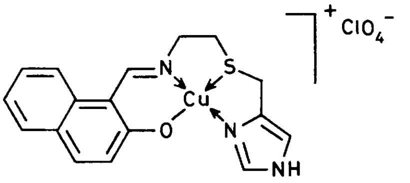
Cationic Complexes of Schiff Bases derived from Hati *and* Hatb.—The ligands (H_2L^3–H_2L^{11} and $H_2L^{3'}$–$H_2L^{11'}$) were prepared by reaction of the amine with the salicylaldehyde and characterised by ^1H and ^{13}C n.m.r., i.r., and m.s. Mononuclear copper(II) complexes were prepared by treating an ethanolic solution of the appropriate ligand with equimolar amounts of $Cu(ClO_4)_2{\cdot}6H_2O$ and methanolic NaOH; or alternatively by a more direct route in which the two reactants are added to a solution of the ligand immediately after formation of the ligand and prior to any isolation. Both routes gave identical products but the latter was less time consuming and gave higher yields.

The i.r. spectra of the complexes of the Hatb-based ligands showed a medium intensity band in the region 3 200—3 250 cm^{-1} attributable to the benzimidazole NH stretching frequency. In the complexes prepared from Hati-based ligands this absorption is located between 3 250 and 3 450 cm^{-1}. These absorptions are generally broad and when associated with a three-component $\nu_3(ClO)$ for the anion at *ca.* 1 100 cm^{-1} suggest similar hydrogen bonding between the pyrrolic-NH of the ligand and an O of the anion as in the structure reported above. An imine band was detected in the 1 600—1 640 cm^{-1} region and comparison with the free base shows that complexation has resulted in a move to lower frequency.

The optical spectra, both in the solid state and in dmso solution, of the Hati-based complexes are very similar to those for the Hatmi-based complexes, again suggesting a close structural similarity (Table 2). Replacement of imidazole by benzimidazole leads to the bands being found at higher wavelength in the Hatb-based complexes. Furthermore in those Hatb-based complexes where there is also a substituent in the 3-position of the salicylaldehyde there is an absorption maximum at slightly longer wavelengths than in the other complexes of the series. Molecular models have indicated that there would be a significant steric interaction between the 3-substituent and a proximal benzimidazole hydrogen atom if the salicylaldehyde and benzimidazole rings were coplanar as the imidazole and benzene rings are in the cation $[Cu(HL^1)]^+$.



	R	X^1	X^2
$[Cu(HL^3)]ClO_4$	H	H	H
$[Cu(HL^4)]ClO_4$	H	H	Br
$[Cu(HL^5)]ClO_4{\cdot}0.5MeOH$	H	NO_2	H
$[Cu(HL^6)]ClO_4$	H	H	NO_2
$[Cu(HL^7)]ClO_4$	H	H	Cl
$[Cu(HL^8)]ClO_4{\cdot}0.5H_2O$	H	Cl	Cl
$[Cu(HL^9)]ClO_4{\cdot}2H_2O$	CH_3	H	H

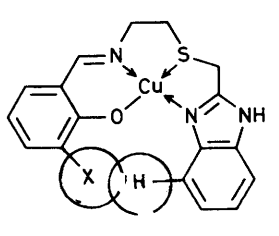


$[Cu(HL^{11})]ClO_4{\cdot}0.5MeOH$

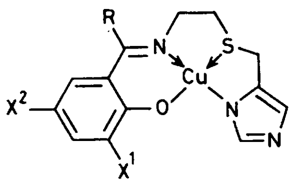
Table 2. Ligand-field maxima for $[Cu(HL)]ClO_4$ and $[Cu(HL')]ClO_4$

	$\lambda_{max.}$/nm	
Complex	Solid[a]	Solution[b]
$[Cu(HL^3)]ClO_4$	649 (sh), 581	636 (193)
$[Cu(HL^4)]ClO_4$	595	638 (207)
$[Cu(HL^5)]ClO_4{\cdot}0.5MeOH$	578	633 (194)
$[Cu(HL^6)]ClO_4$	575	632 (217)
$[Cu(HL^7)]ClO_4$	602	637 (203)
$[Cu(HL^8)]ClO_4{\cdot}0.5H_2O$	676 (sh), 585	643 (179)
$[Cu(HL^9)]ClO_4{\cdot}2H_2O$	581	619 (186)
$[Cu(HL^{11})]ClO_4{\cdot}0.5MeOH$	763, 581	627 (223)
$[Cu(HL^{3'})]ClO_4$	685 (sh), 602	654 (219)
$[Cu(HL^{4'})]ClO_4$	671 (sh), 606	652 (231)
$[Cu(HL^{5'})]ClO_4$	625	671 (166)
$[Cu(HL^{6'})]ClO_4{\cdot}H_2O$	602	652 (226)
$[Cu(HL^{7'})]ClO_4{\cdot}0.5EtOH$	725 (sh), 610	654 (248)
$[Cu(HL^{8'})]ClO_4$	641	657 (238)
$[Cu(HL^{9'})]ClO_4{\cdot}0.5H_2O$	595	642 (242)
$[Cu(HL^{10'})]ClO_4{\cdot}0.5H_2O$	741 (sh), 610	627 (262)
$[Cu(HL^{11'})]ClO_4$	667 (sh), 585	638 (249)

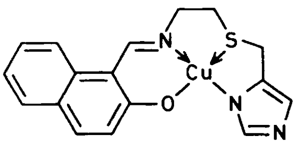
[a] Diffuse reflectance spectrum, sh = shoulder. [b] Dimethyl sulphoxide solution; values in parentheses are the molar absorption coefficient $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$.



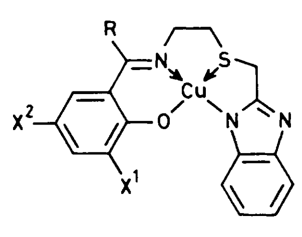
It is likely that to minimise the unfavourable situation the ring systems would move apart, affecting the co-ordination geometry at the metal and therefore the optical spectrum.



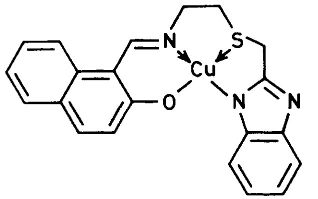
	R	X^1	X^2
$[Cu(L^3)]\cdot 0.25H_2O$	H	H	H
$[Cu(L^4)]\cdot 0.5H_2O$	H	H	Br
$[Cu(L^5)]\cdot 0.5H_2O$	H	NO_2	H
$[Cu(L^6)]\cdot 0.25H_2O$	H	H	NO_2
$[Cu(L^7)]$	H	H	Cl
$[Cu(L^8)]\cdot 0.5CH_3CN$	H	Cl	Cl



$[Cu(L^{11})]\cdot 0.5H_2O$



	R	X^1	X^2
$[Cu(L^{3'})]\cdot 0.5H_2O$	H	H	H
$[Cu(L^{4'})]\cdot H_2O$	H	H	Br
$[Cu(L^{5'})]\cdot 1.5H_2O$	H	NO_2	H
$[Cu(L^{6'})]\cdot H_2O$	H	H	NO_2
$[Cu(L^{7'})]$	H	H	Cl
$[Cu(L^{8'})]\cdot 0.25EtOH$	H	Cl	Cl
$[Cu(L^{10'})]\cdot 0.5CH_3CN$	CH_3	H	CH_3



$[Cu(L^{11'})]\cdot 0.75H_2O$

Table 3. Ligand-field maxima for [Cu(L)] and [Cu(L′)]

Complex	$\lambda_{max.}$/nm *
$[Cu(L^3)]\cdot 0.25H_2O$	654
$[Cu(L^4)]\cdot 0.5H_2O$	625
$[Cu(L^5)]\cdot 0.5H_2O$	667
$[Cu(L^6)]\cdot 0.25H_2O$	641
$[Cu(L^7)]$	637
$[Cu(L^8)]\cdot 0.5CH_3CN$	637
$[Cu(L^{11})]\cdot 0.5H_2O$	625br
$[Cu(L^{3'})]\cdot 0.5H_2O$	667
$[Cu(L^{4'})]\cdot H_2O$	662
$[Cu(L^{5'})]\cdot 1.5H_2O$	709
$[Cu(L^{6'})]\cdot H_2O$	658
$[Cu(L^{7'})]$	667br
$[Cu(L^{8'})]\cdot 0.25EtOH$	667
$[Cu(L^{10'})]\cdot 0.5CH_3CN$	662
$[Cu(L^{11'})]\cdot 0.75H_2O$	667

* Diffuse reflectance spectrum, br = broad.

Neutral Complexes of Schiff Bases derived from Hati *and* Hatb.—A number of plausible routes to the preparation of neutral copper(II) complexes of the Hati- and Hatb-based ligands were investigated with varying degrees of success. Reaction of the cationic complexes with a slight molar excess of methanolic NaOH gave products which were not entirely free from the perchlorate anion. Similar results were obtained by addition of $Cu(ClO_4)_2\cdot 6H_2O$ followed by two equivalents of methanolic NaOH to alcoholic solutions of the ligands. Repeating this latter approach using $Cu(NO_3)_2\cdot 3H_2O$, as both it and $NaNO_3$ are readily soluble in the reaction medium, revealed that the reaction stopped after one deprotonation due to precipitation of the monocationic complex $[Cu(HL)]NO_3$ or $[Cu(HL')]NO_3$. The reaction of copper(II) acetate with the ligand in acetonitrile or acetonitrile containing 20% ethanol gave the neutral complexes [CuL] ($L = L^3$—L^8 or L^{11}) or [CuL′] ($L' = L^{3'}$—$L^{8'}$, $L^{10'}$, or $L^{11'}$) in high yields. All the complexes, except those from the 5-chlorosalicylaldehyde-based ligands, contained occluded solvent molecules. A similar observation was made by Atkins *et al.*[10] for a series of neutral copper(II) complexes of unsymmetrical Schiff-base ligands.

The major difference between the i.r. spectra of the cationic and neutral complexes is the absence of an NH stretching frequency in the latter. Further comparison reveals small changes in the position of the imine absorption: in the neutral benzimidazole complexes this band has generally moved to lower frequency whereas in the imidazole-containing complexes it has moved to higher frequency. It has been suggested that in metal β-diketonate complexes there is an opportunity for (*d*–*p*) π interactions between the metal and ligand and that the chelate ring is best considered as aromatic in character.[16] A similar situation may exist in the six-membered chelated rings of the neutral complexes reported here. If the ligands are considered to be in the xy plane then the most probable mode of π interaction would involve the copper d_{xz} and d_{yz} orbitals. As these are filled they would enable any excess density on the central metal to be back-donated into the aromatic ring system. If this is occurring in the imidazole-based complexes the increase of electron density in these rings could lead to a strengthening of the imine bond; in the benzimidazole complexes the ability of the benzene ring to attract electron density could lead to a weakening of the imine bond.

The optical spectra of the neutral benzimidazole complexes were recorded in the solid state only as these complexes were insoluble in a wide range of solvents; for comparison the imidazolate complexes were similarly recorded (Table 3). The spectra were often broad but the *d*–*d* band has generally moved to lower energy as compared with the corresponding cationic complex. The similarity in spectra suggests a similarity in structure type. It has not yet been possible to grow crystals suitable for *X*-ray analysis, but it is likely that the structures of the neutral complexes are closely related to that of the molecular cation $[Cu(HL^1)]^+$.

A preliminary communication of the utility of the neutral complexes in the preparation of homo- and hetero-binuclear complexes containing endogenous imidazolate bridges has been presented;[15] further work to establish the generality of the reaction is in progress.

Experimental

Microanalyses were performed by the University of Sheffield Microanalytical Service (Table 4). M.s. were recorded on a

Table 4. Analytical data

Complex	Found (%)				Calc. (%)			
	C	H	N	Cl	C	H	N	Cl
$[Cu(HL^1)]ClO_4$	38.4	3.7	9.5	8.0	38.5	3.7	9.6	8.1
$[Cu(HL^2)]ClO_4\cdot0.5H_2O$[a]	32.1	3.2	7.9	6.8	32.0	3.1	8.0	6.7
$[Cu(HL^3)]ClO_4$	36.7	3.5	9.7	8.5	36.9	3.3	9.9	8.4
$[Cu(HL^4)]ClO_4$	41.4	2.8	8.2	7.9	41.1	2.6	8.4	7.1
$[Cu(HL^5)]ClO_4\cdot0.5MeOH$[b]	33.8	3.2	11.7	7.7	33.5	3.1	11.6	7.3
$[Cu(HL^6)]ClO_4$	33.5	2.9	11.9	7.8	33.3	2.8	12.0	7.6
$[Cu(HL^7)]ClO_4$	33.8	3.2	9.0	15.2	34.1	2.9	8.4	15.5
$[Cu(HL^8)]ClO_4\cdot0.5H_2O$	30.9	2.5	8.5	20.9	31.2	2.6	8.4	21.2
$[Cu(HL^9)]ClO_4\cdot2H_2O$	35.6	3.9	9.2	8.5	35.5	4.2	8.9	7.5
$[Cu(HL^{11})]ClO_4\cdot0.5MeOH$	43.1	3.5	8.2	7.5	42.9	3.7	8.6	7.2
$[Cu(HL^{3'})]ClO_4$	43.2	3.7	8.7	7.6	43.1	3.4	8.9	7.5
$[Cu(HL^{4'})]ClO_4$[c]	37.1	2.9	7.5	6.3	37.0	2.7	7.6	6.4
$[Cu(HL^{5'})]ClO_4$	39.2	2.9	10.7	7.0	39.4	2.9	10.8	6.8
$[Cu(HL^{6'})]ClO_4\cdot H_2O$	38.4	3.1	10.8	6.6	38.1	3.2	10.4	6.6
$[Cu(HL^{7'})]ClO_4\cdot0.5EtOH$	40.7	3.2	8.2	13.5	40.7	3.4	7.9	13.4
$[Cu(HL^{8'})]ClO_4$	37.4	2.8	7.6	19.6	37.6	2.6	7.7	19.6
$[Cu(HL^{9'})]ClO_4\cdot0.5H_2O$	43.6	3.8	8.4	7.4	43.6	3.9	8.5	7.1
$[Cu(HL^{10'})]ClO_4\cdot0.5H_2O$	44.8	4.3	8.1	7.2	44.7	4.2	8.2	7.0
$[Cu(HL^{11'})]ClO_4$	48.2	3.8	7.5	7.2	48.2	3.5	8.0	6.8
$[Cu(L^3)]\cdot0.25H_2O$	47.8	4.3	13.0		47.7	4.2	12.8	
$[Cu(L^4)]\cdot0.5H_2O$[d]	37.9	3.3	10.0		38.0	3.2	10.2	
$[Cu(L^5)]\cdot0.5H_2O$	41.3	3.6	15.0		41.4	3.5	14.9	
$[Cu(L^6)]\cdot0.25H_2O$	42.3	3.4	14.9		42.0	3.4	15.0	
$[Cu(L^7)]$	43.6	3.5	11.8	9.8	43.7	3.4	11.8	9.9
$[Cu(L^8)]\cdot0.5CH_3CN$	40.7	3.4	11.6	17.1	40.8	3.1	11.9	17.2
$[Cu(L^{11})]\cdot0.5H_2O$	53.1	4.1	10.8		53.5	4.2	11.0	
$[Cu(L^{3'})]\cdot0.5H_2O$	53.5	4.3	10.8		53.5	4.2	11.0	
$[Cu(L^{4'})]\cdot H_2O$[e]	43.5	3.3	8.7		43.5	3.4	9.0	
$[Cu(L^{5'})]\cdot1.5H_2O$	46.2	3.6	12.7		45.9	3.0	12.6	
$[Cu(L^{6'})]\cdot H_2O$	47.1	3.6	12.7		46.8	3.7	12.9	
$[Cu(L^{7'})]$	50.0	3.9	10.4	8.7	50.1	3.5	10.3	8.7
$[Cu(L^{8'})]\cdot0.25EtOH$	46.3	3.5	9.0	16.0	46.4	3.2	9.3	15.6
$[Cu(L^{10'})]\cdot0.5CH_3CN$	57.1	4.9	11.2		57.0	4.9	11.6	
$[Cu(L^{11'})]\cdot0.75H_2O$	57.9	4.2	9.8		57.8	4.3	9.6	

Br Found (%), calc. (%): [a] 15.4, 15.2; [b] 15.9, 15.9; [c] 14.2, 14.5; [d] 19.7, 19.5; [e] 17.0, 17.0.

Kratos MS25 spectrometer. I.r. spectra were recorded, as KBr discs or liquid films, using a Perkin-Elmer 297 spectrophotometer. Visible absorption spectra were obtained using a Perkin-Elmer Lambda 3 spectrophotometer (solutions) and a Pye Unicam SP 700 (diffuse reflectance spectra of solids). Hydrogen-1 and ^{13}C n.m.r. spectra were run on a Bruker WH 250-MHz multinuclear spectrometer.

4-[(2-Aminoethyl)thiomethyl]-5-methylimidazole dihydrochloride was supplied, as a gift, by Dr. J. C. Emmett of Smith, Kline, and French Research Ltd. 2-[(2-Aminoethyl)thiomethyl]-benzimidazole dihydrobromide was prepared from 2-hydroxymethylbenzimidazole and cysteamine hydrochloride by the method of Durant *et al.*,[17] as was 4(5)-[(2-aminoethyl)-thiomethyl]imidazole dihydrobromide prepared from 4(5)-hydroxymethylimidazole[18] and cysteamine hydrochloride.

Schiff-base Formation.—The dihydrobromide of the aminothioetherimidazole (1 mmol) was suspended in absolute ethanol (20 cm^3) and treated with methanolic NaOH (2 cm^3; 1 mol dm^{-3}) with stirring. A clear colourless solution resulted within a few minutes and, after stirring at ambient temperature for a further 20 min, was evaporated *in vacuo* to leave a white solid residue. Extraction with $CHCl_3$ (5 × 5 cm^3) and filtration gave a clear solution of the free base. The solvent was removed *in vacuo* and replaced by absolute ethanol (15 cm^3) prior to Schiff-base formation.

Addition of a solution of the required salicylaldehyde derivative (1 mmol) in absolute ethanol (5 cm^3) with stirring to an ethanolic solution of the aminothioetherimidazole as prepared above gave clear yellow, or orange, solutions which were gently refluxed for intervals between 15 and 60 min. Evaporation of the solution *in vacuo* gave either oils which slowly crystallised, or solids. The products were dried *in vacuo* prior to use in complexation reactions. The presence of occluded solvent in the samples did not give completely reproducible microanalytical data; the compounds were characterised by n.m.r.[19] prior to use.

Monocationic Copper(II) *Complexes.*—A solution of the appropriate ligand (1 mmol) was prepared by either dissolving the required amount of the ligand in absolute ethanol (20 cm^3) or by preparing the ligand *in situ* from its precursors. Solid $Cu(ClO_4)_2\cdot6H_2O$ (1 mmol) was then added to the ligand solution with stirring and the reaction mixture stirred under reflux for *ca.* 5 min, after which methanolic NaOH (1 cm^3; 1 mol dm^{-3}) was added. Reflux and stirring were maintained for a further 5 min and the reaction was then cooled to ambient temperature. The product was removed by filtration, washed (absolute ethanol, diethyl ether), and dried *in vacuo* overnight.

Neutral Copper(II) *Complexes.*—A solution of the appropriate ligand (1 mmol) was prepared by either dissolving the required amount of the ligand in acetonitrile (20 cm^3) or by preparing the ligand *in situ*, as described above, and then replacing the ethanol with acetonitrile (20 cm^3) prior to

Table 5. Atomic positional parameters with estimated standard deviations for $[Cu(HL^1)]ClO_4$*

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.047 25(14)	0.029 06(13)	−0.126 21(15)	C(2)	−0.322 1(10)	−0.057 7(11)	−0.207 1(9)
Cl(1)	0.199 32(31)	−0.550 25(25)	0.118 06(24)	C(3)	−0.428 8(11)	−0.007 2(12)	−0.247 7(9)
S(1)	0.210 4(6)	0.123 7(5)	−0.031 6(4)	C(4)	−0.433 8(10)	0.111 9(12)	−0.265 5(9)
S(2)	0.264 7(5)	0.103 3(5)	−0.143 6(5)	C(5)	−0.328 6(10)	0.181 3(11)	−0.246 6(9)
O(1)	−0.112 1(7)	−0.041 5(7)	−0.152 3(7)	C(6)	−0.215 2(10)	0.132 2(10)	−0.206 6(8)
O(2)	0.196 9(24)	−0.521 8(12)	0.027 4(11)	C(7)	−0.110 6(10)	0.211 8(9)	−0.188 5(8)
O(3)	0.224 1(14)	−0.666 9(8)	0.132 9(8)	C(8)	0.096 0(11)	0.278 6(10)	−0.142 6(10)
O(4)	0.072 3(13)	−0.532 9(14)	0.134 7(16)	C(9)	0.216 3(15)	0.227 9(12)	−0.106 3(14)
O(5)	0.265 7(16)	−0.474 0(12)	0.165 8(14)	C(10)	0.326 2(10)	0.005 0(10)	−0.054 8(10)
N(1)	−0.001 3(8)	0.184 7(7)	−0.154 5(7)	C(11)	0.256 2(10)	−0.108 5(10)	−0.053 8(8)
N(2)	0.189 0(9)	−0.288 0(8)	−0.042 6(7)	C(12)	0.294 2(11)	−0.217 4(10)	−0.028 9(8)
N(3)	0.128 5(8)	−0.113 6(7)	−0.084 9(6)	C(13)	0.421 8(12)	−0.261 5(12)	0.007 3(9)
C(1)	−0.210 2(10)	0.011 8(10)	−0.187 9(9)	C(14)	0.093 2(10)	−0.224 4(9)	−0.076 6(8)

* Atoms S(1) and S(2) are the two equally populated disorder sites for the sulphur. Atoms Cl(1), O(2)–O(5) constitute the perchlorate anion.

complex formation. Solid $Cu(O_2CMe)_2 \cdot H_2O$ (1 mmol) was added to the ligand solution with stirring and the reaction mixture stirred under gentle reflux for *ca.* 30 min. The mixture was allowed to cool and the product removed by filtration. The product was washed with acetonitrile, ethanol, and diethyl ether and then dried *in vacuo* overnight.

Crystal Structure Determination of $[Cu(HL^1)]ClO_4$.—*Crystal data.* $C_{14}H_{16}ClCuN_3O_5S$, $M = 437.35$, crystallises by slow evaporation of a hot solution of ethanol as deep red elongated bricks with a rhomboid cross section, crystal dimensions 0.43 × 0.22 × 0.22 mm, monoclinic, $a = 10.32(3)$, $b = 11.41(3)$, $c = 14.34(4)$ Å, $\beta = 89.33(5)°$, $U = 1\,689(8)$ Å^3, $D_m = 1.71$, $D_c = 1.720$ g cm^{-3}, $Z = 4$, space group $P2_1/c$ (C^5_{2h}, no. 14), Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 16.04 cm^{-1}, and $F(000) = 828$.

Three-dimensional *X*-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the ω scan method. The 1 196 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. The sulphur was found to be equally disordered between two sites corresponding to two different conformations for the central chelate ring. Since the sites were well separated (1.71 Å), no constraints were applied during refinement. Hydrogen atoms were detected and placed in calculated positions [C–H 0.96, N–H 0.96 Å, C–C–H(methyl) 112°]. Those hydrogens on atoms C(9), C(10), and C(13) were inserted with half occupancy to allow for the sulphur disorder and for the methyl rotational disorder. The contributions of the hydrogen atoms were included in structure factor calculations ($B = 7.0$ Å^2) but no refinement of positional parameters was permitted. Refinement converged at R 0.0587 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of copper, chlorine, and sulphur. Table 5 lists the atomic positional parameters with estimated standard deviations. Scattering factors were taken from ref. 20; unit weights were used throughout the refinement; computer programs formed part of the Sheffield *X*-ray system.

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

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