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Monomeric and Dimeric Copper(II) Complexes of a Pyrrole-Containing Tridentate Schiff-Base Ligand

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Three copper(II) complexes of $(L^1)^-$, $[CuL^1Cl]$ (**1**), $[CuL^1Br]_n$ (**2**) and $[Cu_2(L^1)_2(\mu_{1,3}\text{-}NCS)_2]$ (**3**), and two copper(II) complexes of HL^1, $[Cu(HL^1)X_2]$ ($X = Cl^-$, **4**; $X = Br^-$, **5**), have been prepared and characterised [where HL^1 is the Schiff-base ligand derived from pyrrole-2-carbaldehyde and 2-aminomethylpyridine]. The removal of a chloride ion and deprotonation of $[Cu(HL^1)Cl_2]$ (**4**) to form $[CuL^1Cl]$ (**1**) worked well. However, attempts to protonate $[CuL^1Cl]$ with HCl to re-form $[Cu(HL^1)Cl_2]$ were not successful. X-ray structure determinations revealed that **1** is a N_3Cl-coordinated square-planar copper(II) monomer $[CuL^1Cl]$, whereas **3** is a doubly end-to-end thiocyanate-bridged square-pyramidal copper(II) dimer $[Cu_2(L^1)_2(\mu_{1,3}\text{-}NCS)_2]$. The structure determinations on **4** and **5** showed that in both cases the copper(II) ion is in a distorted square-planar N_2X_2 environment, with the pyrrole NH remaining non-deprotonated and uncoordinated. Variable-temperature magnetic susceptibility investigations carried out on the end-to-end thiocyanate doubly bridged square-pyramidal copper(II) dimer **3** showed that no magnetic coupling occurs between the two copper(II) ions; it exhibits Curie-like magnetic behaviour.

Introduction

Over the years much effort has gone into the investigation of complexes of a wide range of acyclic Schiff-base ligands, in particular into pyridine-containing systems. Much less is known about complexes of pyrrole-analogues of such ligands, despite the potentially interesting similarities to porphyrins. Recently, our focus has been on the copper(II) chemistry of N_3 tridentate Schiff-base ligands, in particular the mixed pyrrole-pyridine ligands HL^1 and HL^2 (Figure 1). These are closely related to the pyridine-pyridine ligands, L^A, L^B and L^C (Figure 1) which have been well studied,[1] and summarised in our recent publication.[2] As seen from that summary, the complexes of the ligands L^A, L^B and L^C, together with those obtained with other closely related tridentate Schiff-base ligands,[3,4] indicate that the use of less flexible tridentate ligands tends to result in the formation of monomeric and dimeric complexes while the use of more flexible tridentate ligands tends to give rise to dimeric or polymeric complexes. These dimeric and polymeric complexes can exhibit interesting magnetic behaviour.

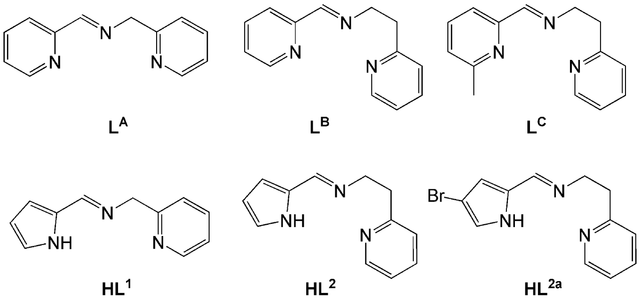

Figure 1. Selection of tridentate N_3 Schiff-base ligands, including those used in this research.

In contrast to the above pyridine-imine-pyridine tridentate ligand systems, a search of the Cambridge Structural Database [CSD, Version 5.30 (February 2009)][5] revealed that of the 240 or so complexes of 2-iminopyrrole-based ligands, only 10% involved a tridentate binding mode. A similar result from an earlier search prompted us to investigate the coordination chemistry of the tridentate 2-iminopyrrole Schiff-base ligands HL^1 and HL^2 which are expected to coordinate as monoanionic ligands $(L^1)^-$ and $(L^2)^-$. These two homologous 2-iminopyrrole tridentate Schiff-base ligands are analogues of the neutral pyridine-pyridine Schiff-base ligands L^A and L^B, with $(L^1)^-$ being less flexible than $(L^2)^-$. As seen for L^A and L^B this difference in flexibility is expected to influence the nature of the product, e.g. the formation of a mono-, di- or polymeric complex.

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Recently, we reported a series of halide- or pseudohalide-bridged dimeric copper(II) complexes of $(L^2)^-$, $[Cu_2(L^2)_2(\mu\text{-}X)_2]$ (X = Cl^-, **6**; X = Br^-, **7**; X = N_3^-, **8**; X = NCS^-, **9**), as well as an unusual bromo-bridged 1D polymeric copper(II) complex of the brominated pyrrole derivative $(L^{2a})^-$, $[CuL^{2a}(\mu\text{-}Br)]_\infty$ (**10**).[2] Crystal structures of the complexes **6**–**8** and **10** indicate that use of the ethylene-linked ligand $(L^2)^-$ and its brominated form $(L^{2a})^-$ leads to the formation of dimeric or 1D-chain polymeric copper(II) complexes. Weak antiferromagnetic exchange is observed for complexes **6**–**8** and **10**. No other complexes of $(L^2)^-$ or HL^2 have been reported in the literature.

However, since we initiated our studies with the methylene-linked analogue, HL^1, a copper(I)[6] complex of $(L^1)^-$ and heavy-metal (ruthenium, rhodium and iridium)[7] complexes of both $(L^1)^-$ and HL^1 have been published. Specifically, Floriani and co-workers have used $(L^1)^-$ to synthesise complexes and organometallic compounds of ruthenium(II).[7] The rhodium(I) and iridium(I) complexes of the amine analogue of HL^1 have also been studied, by Gal and co-workers, in order to investigate their potential as catalysts for the polymerisation of phenylacetylene.[4] More recently, a copper(I) complex of $(L^1)^-$ has been reported and the X-ray crystal structure analysis carried out on the complex shows that it is an unusual asymmetric copper(I) dimer with two-coordinate and four-coordinate copper(I) sites.[6] No other transition-metal complexes of $(L^1)^-$ have been reported in the literature to date.

The aim of the present study was to access a family of copper(II) complexes of the methylene-linked ligand, HL^1, in order to enable a comparison with the dimeric copper(II) complexes **6**–**9** that resulted from the use of the analogous ethylene-linked ligand HL^2.[2] Here, we detail the synthesis, spectral and structural characterisation of the copper(II) complexes of $(L^1)^-$ in the form of $[CuL^1Cl]$ (**1**), $[CuL^1Br]_n$ (**2**) and $[Cu_2(L^1)_2(\mu_{1,3}\text{-}NCS)_2]$ (**3**) and of HL^1 in the form of $[Cu(HL^1)X_2]$ (X = Cl^-, **4**; X = Br^-, **5**). The magnetic properties of the structurally characterised copper(II) dimer, $[Cu_2(L^1)_2(\mu_{1,3}\text{-}NCS)_2]$ (**3**), are also presented.

Results and Discussion

Synthesis of Copper Complexes of HL^1 and $(L^1)^-$

The ligand HL^1, a homologue of HL^2, is also potentially a tridentate Schiff-base ligand containing both a pyridine and a pyrrole moiety. As seen for HL^2, the pyrrole NH moiety in HL^1 can be deprotonated in the presence of a base and this leads to tridentate coordination of $(L^1)^-$ to the metal ion. Pure HL^1 was readily prepared at room temperature in ethanol in close to quantitative yield, without any need for recrystallisation.[4,7]

The copper(II) complexes of the deprotonated tridentate ligand $(L^1)^-$, $[CuL^1Cl]$ (**1**), $[CuL^1Br]_n$ (**2**) and $[Cu_2(L^1)_2(\mu_{1,3}\text{-}NCS)_2]$ (**3**), were synthesised in the presence of a base, triethylamine, while in the absence of a base complexes of the neutral bidentate ligand HL^1, $[Cu(HL^1)Cl_2]$ (**4**) and $[Cu(HL^1)Br_2]$ (**5**), precipitated from the reaction solutions. It is worth mentioning that due to the weak acidity of pyrrole it is not unusual that the pyrrole NH group of a pyrrole-containing ligand remains non-deprotonated and uncoordinated when the ligand is bound to a metal ion in the absence of base.[8]

The order of addition used for the preparation of $[CuL^1Cl]$ (**1**) was modified to ensure that analytically pure olive green solid $[CuL^1Br]_n$ (**2**) precipitated from that reaction solution. As was seen for the preparation of $[Cu_2(L^2)_2(\mu\text{-}Br)_2]$ (**7**),[2] the ethylene-linked analogue, the wrong order of addition leads to a crude product contaminated by impurities involving the brominated-ligand, and this appeared to also be an issue with the methylene-linked ligand.

Microanalysis of **1**–**3** showed the stoichiometry to be $[CuL^1X]_n$ (X = Cl^-, Br^-, NCS^-). The X-ray crystal structure determinations reveal that complex **1** is a monomer, $[CuL^1Cl]$ (Figure 2), while complex **3** is an end-to-end doubly thiocyanate-bridged dimer, $[Cu_2(L^1)_2(\mu_{1,3}\text{-}NCS)_2]$ (Figure 3). Due to the likely similarity between the chloro and bromo complexes, **1** and **2**, the bromo complex **2** may also be a monomer, $[CuL^1Br]_n$ $n = 1$, but this (i.e. n) cannot be verified without single crystals and an X-ray structure determination, and these were not forthcoming, so whilst the empirical formula is clear, the molecular formula is not.

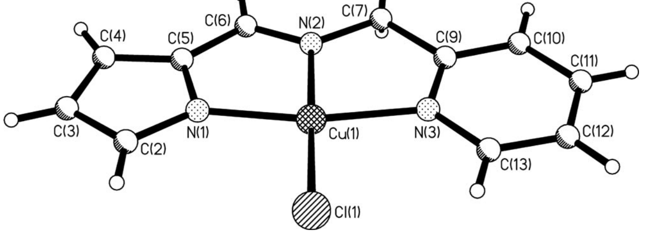

Figure 2. Perspective view of $[CuL^1Cl]$ (**1**).

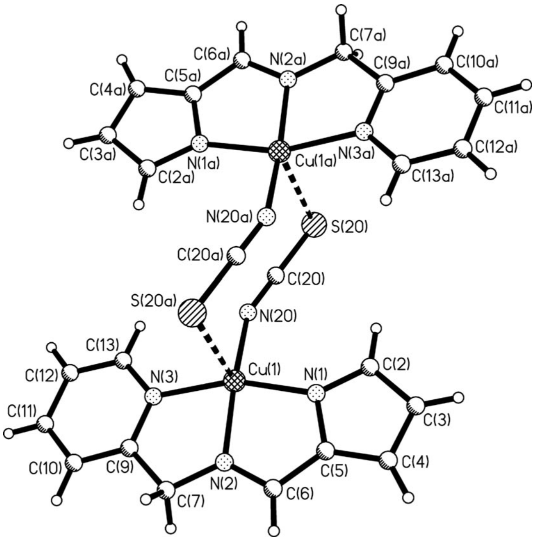

Figure 3. Perspective view of the dimeric copper(II) complex $[Cu_2(L^1)_2(\mu_{1,3}\text{-}NCS)_2]$ (**3**). Symmetry operation a is $-x + 1$, $-y + 1$, $-z + 1$.

In contrast to the reactions with HL^2, simply mixing HL^1 with either copper(II) chloride dihydrate or copper(II) bromide in methanol resulted in green precipitates. Microanalysis (C, H, N, X) carried out on these solids revealed the stoichiometry to be $[Cu(HL^1)X_2]_n$ ($X = Cl^-$, **4**; $X = Br^-$, **5**) and N–H stretching vibrations at 3240 and 3266 cm^{-1}, respectively, in the infrared spectra indicated that the pyrrole NH of the ligand was not deprotonated. X-ray structure determinations carried out on both of these complexes, **4** and **5**, conclusively confirm that the pyrrole NH groups remain non-deprotonated and uncoordinated (Figure 4).

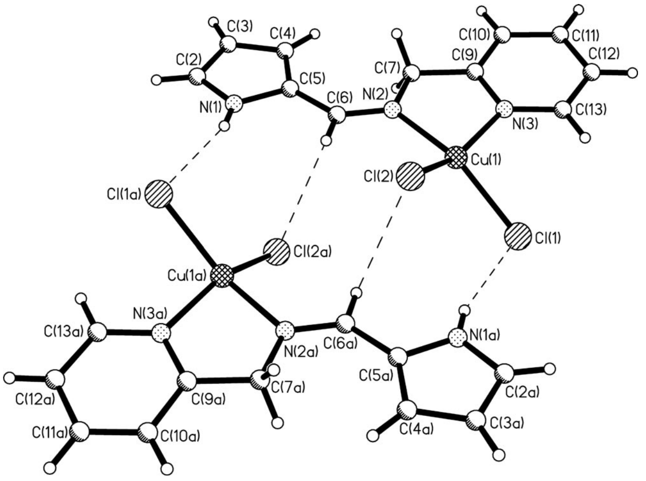

Figure 4. Perspective view of the hydrogen-bonded dimeric copper(II) complex $[Cu(HL^1)Cl_2]_2$ (**4**). The bromo complex, **5**, is isostructural.

It is intriguing that attempts to prepare copper(II) complexes of the neutral ethylene-linked ligand HL^2 were unsuccessful (no clean complexes were isolated) whereas the copper(II) complexes of the neutral methylene-linked ligand HL^1, $[Cu(HL^1)X_2]$, were so readily prepared. This is presumably due to a combination of factors such as solubility, chelate ring size and hydrogen bond complementarity.

Interconversion between the complexes $[Cu(HL^1)Cl_2]$ (**4**) and $[CuL^1Cl]$ (**1**) was attempted. Gal and co-workers had reported that the reaction of the rhodium(I) and iridium(I) complexes of the amine analogue of HL^1 in its neutral form with an excess of aqueous Na_2CO_3 resulted in deprotonation of the pyrrole NH and coordination of the resulting deprotonated pyrrole nitrogen atom to the metal ions.[4] This method was used in attempts to convert $[Cu(HL^1)Cl_2]$ to $[CuL^1Cl]$. However, despite using a range of different bases, including Na_2CO_3, NaOH and triethylamine, this was unsuccessful. On further investigation it was found that for the conversion to occur one of the two chloride ions must be removed first. The complex cation $[Cu(HL^1)Cl]^+$ can be produced by using one equivalent of silver tetrafluoroborate to remove one equivalent of the coordinated chloride ion from $[Cu(HL^1)Cl_2]$. This cation is then reacted with one equivalent of triethylamine in methanol and the resulting deprotonated pyrrole nitrogen atom coordinates to the copper(II) ion to complete the conversion and give the complex of the deprotonated ligand, $[CuL^1Cl]$. The dark green product obtained is analytically pure, and the band at 3240 cm^{-1} in $[Cu(HL^1)Cl_2]$ is absent, confirming that the deprotonation of the ligand has occurred. Also, the imine bond vibration shifts from 1621 cm^{-1} for $[Cu(HL^1)Cl_2]$ to 1589 cm^{-1} for $[CuL^1Cl]$, and the remainder of the IR spectrum is identical to that of **1**, providing further evidence that the conversion has been successful. An attempt to convert $[CuL^1Cl]$ back to $[Cu(HL^1)Cl_2]$ using HCl was unsuccessful. Acidifying a complex is always going to be more difficult, especially when it involves a Schiff-base ligand.

An attempt to make a 1:1 copper(I) complex of the bidentate neutral HL^1, using tetraacetonitrilecopper(I) tetrafluoroborate, tetraethylammonium chloride and HL^1 in dry acetonitrile under argon, resulted instead in the precipitation of dark green microcrystals of analytically pure **1**. The observed oxidation of copper(I) to copper(II) is presumably due to the presence of trace amounts of oxygen, as strict Schlenk conditions were not employed. This was not pursued further.

Infrared Spectra

The infrared spectra of the complexes of the deprotonated ligand $(L^1)^-$ and non-deprotonated ligand HL^1, **1**–**5**, have many common characteristics, and also have features in common with the complexes of $(L^2)^-$, **6**–**10**, as expected. The imine bands occur at ca. 1590 cm^{-1} for the complexes of $(L^1)^-$, **1**–**3**, very close to the values found for the dimeric complexes of $(L^2)^-$, **6**–**9**. As expected, the imine stretching vibrations for the complexes of neutral HL^1, **4** and **5**, are at higher frequencies, ca. 1620 cm^{-1}. The band due to the thiocyanate ion C≡N stretch in $[Cu_2(L^1)_2(\mu_{1,3}\text{-NCS})_2]$ (**3**) was observed at 2095 cm^{-1}. As discussed for the previously reported complex $[Cu_2(L^2)_2(\mu_{1,3}\text{-NCS})_2]$ (**9**),[2] this frequency suggests that the thiocyanate ion may act as end-to-end bridge, although the S-bound mode cannot be ruled out. However, the X-ray crystal structure determination carried out on **3** unambiguously confirms that **3** is a doubly end-to-end thiocyanate-bridged dimer (Figure 3). For the complexes of neutral HL^1, $[Cu(HL^1)X_2]$ ($X = Cl^-$, Br^-), the pyrrole NH stretch occurred at 3240 cm^{-1} for $[Cu(HL^1)Cl_2]$ and 3266 cm^{-1} for $[Cu(HL^1)Br_2]$, clear evidence that the ligand is not deprotonated. This has subsequently been confirmed by the X-ray crystal structure analyses carried out on **4** and **5**.

Mass Spectra

The electrospray mass spectra of the complexes $[CuL^1Cl]$ (**1**) and $[CuL^1Br]_n$ (**2**) show a common peak, the fragment $[CuL^1]^+$, which is associated with the loss of their respective coligands, chloride or bromide ions. For **1** a peak at 531, corresponding to $[Cu_2(L^1)_2Cl]^+$, suggests that the formation of a chloride-bridged dimeric copper(II) complex of $(L^1)^-$, $[Cu_2(L^1)_2(\mu\text{-Cl})_2]$, is possible, at least in the mass spectrometer. The electrospray mass spectrum of $[Cu_2(L^1)_2(\mu_{1,3}\text{-NCS})_2]$ (**3**) shows a peak corresponding to $[Cu_2(L^1)_2(\mu_{1,3}\text{-}$

NCS)]$^+$, evidence which supports the presence of a dimeric complex and this has been confirmed by an X-ray crystal structure determination (Figure 3). The electrospray mass spectra of the complexes of HL^1, [Cu(HL^1)Cl$_2$] (**4**) and [Cu(HL^1)Br$_2$] (**5**), have similar fragmentation patterns to one another. They both have three peaks corresponding to [Cu(HL^1)X]$^+$, [CuL^1(CH$_3$CN)]$^+$ and [Cu$_2$(HL^1)$_2$X$_3$]$^+$ (X = Cl$^–$, Br$^–$). The last of these fragments is a sign of the presence of dimeric complexes, as has been observed in the X-ray structures of **4** and **5** (Figure 4).

UV/Vis Spectra

The UV/Vis spectra of the two, probably monomeric, copper(II) complexes of (L^1)$^–$, [CuL^{1}Cl] (**1**) and [CuL^{1}Br]$_n$ (**2**), in methanol, show the copper(II) d–d transition[9] at 617 nm (ε = 257 dm^3 mol$^{–1}$ cm$^{–1}$) for **1** and 610 nm (ε = 242 dm^3 mol$^{–1}$ cm$^{–1}$) for **2**. The thiocyanate-bridged dimeric copper(II) complex [Cu$_2$(L^1)$_2$(μ$_{1,3}$-NCS)$_2$] (**3**) exhibits a band, in methanol, at 617 nm (ε = 133 dm^3 mol$^{–1}$ cm$^{–1}$) due to the copper(II) d–d transition.[9,10] The two copper(II) complexes of HL^1, [Cu(HL^1)Cl$_2$] (**4**) and [Cu(HL^1)Br$_2$] (**5**), have similar UV/Vis spectra to one another. A broad, weak absorption band, in methanol, at 709 nm (ε = 94 dm^3 mol$^{–1}$ cm$^{–1}$) for **4** and 710 nm (ε = 138 dm^3 mol$^{–1}$ cm$^{–1}$) for **5** is attributed to the copper(II) d–d transition. The red shift in these bands relative to the corresponding absorption (610–620 nm) observed for the complexes of the deprotonated ligand (L^1)$^–$, **1** and **2**, indicates an overall decrease in the ligand field strength around each copper(II) centre. In addition to this visible d–d transition, three intense bands are found in the range of 240–370 nm (ε = 4.6×10^3 to 1.40×10^4 dm^3 mol$^{–1}$ cm$^{–1}$) for all five complexes, **1**–**5**, due to either charge transfer or π–π* transitions.

X-ray Crystal Structures

[CuL^{1}Cl] (1)

Green plate crystals of [CuL^{1}Cl] were obtained by the slow diffusion of diethyl ether vapour into a dichloromethane solution of the complex and the X-ray crystal structure determined (Figure 2, Table 1).

Table 1. Selected bond lengths [Å] and angles [°] for [CuL^{1}Cl] (**1**).

Cu(1)–N(1)	1.946(2)	N(1)–Cu(1)–N(2)	82.14(9)
Cu(1)–N(2)	1.962(2)	N(1)–Cu(1)–N(3)	162.35(9)
Cu(1)–N(3)	2.021(2)	N(2)–Cu(1)–N(3)	80.55(9)
Cu(1)–Cl(1)	2.2362(9)	N(1)–Cu(1)–Cl(1)	97.91(7)
		N(2)–Cu(1)–Cl(1)	176.55(7)
		N(3)–Cu(1)–Cl(1)	99.59(7)

The structure consists of isolated monomeric [CuL^{1}Cl] molecules. The copper atom is bound to three nitrogen atoms (comprised of one deprotonated pyrrole nitrogen donor, one pyridine nitrogen donor and one imine nitrogen donor) of the tridentate ligand (L^1)$^–$ and to one chloride ion, giving an N$_3$Cl coordination sphere. The geometry of the coordination polyhedron around the copper(II) ion is very close to square planar (Σangles at Cu: 360.19°) and the copper atom is located just 0.0071(9) Å out of the mean plane defined by the N$_3$Cl donor atoms. The two *cis* N–Cu–N angles are very similar [80.55(9) and 82.14(9)°]. Both are significantly smaller than 90°, as expected when both are part of five-membered, pyrrole-imine or pyridine-imine, chelate rings. The two *cis* N–Cu–Cl angles are similar to one another [97.91(7) and 99.59(7)°] (Table 1).

The molecule is quite flat, with a maximum deviation from the mean plane defined by the N$_3$Cl donor atoms, of just 0.1838 Å, for C(3). In addition there is a weak intermolecular π–π interaction between the nearly parallel (dihedral angle of 3.3°) pyrrole ring of one molecule and a pyridine ring of a neighbouring molecule.

The ligands (L^1)$^–$ and (L^2)$^–$ are clearly very closely related, however, complexation of them with CuCl$_2$ gives two different structural types, the monomer [CuL^{1}Cl] (**1**) (Figure 2) and the dimer [Cu$_2$(L^2)$_2$(μ-Cl)$_2$] (**6**),[2] respectively. The only difference between the ligands is that there is one carbon atom between the pyridine ring and imine nitrogen in the ligand (L^1)$^–$ rather than two carbon atoms in the ligand (L^2)$^–$. Thus, the ligand (L^1)$^–$ is less flexible than (L^2)$^–$. It is probably the reduced flexibility and greater steric constraint of (L^1)$^–$ that results in the formation of the monomeric copper(II) complex. The Cu(1)–N(1) and Cu(1)–N(3) bond lengths in [CuL^{1}Cl] are the same, within experimental error, as those observed for the dimeric complex [Cu$_2$(L^2)$_2$(μ-Cl)$_2$]. However, consistent with the four coordination of copper(II) in [CuL^{1}Cl], the Cu(1)–N(2) and Cu(1)–Cl(1) distances are considerably shorter than those in the five coordinate copper(II) complex [Cu$_2$(L^2)$_2$(μ-Cl)$_2$], and, not surprisingly, the same trend was recently reported for the 2-acetylpyrrole analogues, [CuL^{1Me}Cl], 1.956(3) and 2.2319(12) Å, respectively,[11] and [Cu$_2$(L^{2Me})$_2$(μ-Cl)$_2$], 2.009(3) and 2.3139(10) Å, respectively.[12] The Cu–N(1) (pyrrole nitrogen) is very similar to that reported for related copper(II) complexes.[2,11–14] Cu–N (pyridine nitrogen) bonds are usually 2.00–2.05 Å long,[15] so the Cu–N(3) (pyridine nitrogen) distance in this complex [2.021(2) Å] is normal.

[Cu$_2$(L^1)$_2$(μ$_{1,3}$-NCS)$_2$] (3)

Blue-green plate crystals of [Cu$_2$(L^1)$_2$(μ$_{1,3}$-NCS)$_2$] were obtained by the slow diffusion of diethyl ether vapour into a dichloromethane solution of the complex and the X-ray crystal structure determined (Figure 3, Table 2). The asymmetric unit contains half of the neutral dimeric molecule and the other half is generated by a centre of inversion. The two copper(II) ions are doubly bridged by two thiocyanate ions in an end-to-end fashion. Each copper atom is bound to three nitrogen atoms of the monodeprotonated tridentate ligand (L^1)$^–$ and two bridging thiocyanate groups (one via N and the other via S), giving an N$_4$S coordination sphere. According to the Addison τ value of 0.10[16] the coordination polyhedron around each copper(II) ion can be described as a distorted square pyramid. The basal coordination sites are occupied by the three nitrogen atoms of the ligand and one nitrogen atom [N(20)] from one bridging thiocyanate group, at a distance of 1.958(3) Å, while the apical position is occupied by a sulfur atom [S(20a)] of the other bridging thiocyanate group at a distance of 2.8283(10) Å. The three Cu–N basal bond lengths [excluding Cu–N(20)] are almost the same, within experimental error, as those observed for the monomeric copper(II) complex [CuL^1Cl]. However, of these three Cu–N basal distances, the shortest bond does not occur between the copper atom and the deprotonated negatively charged pyrrole nitrogen atom but between the copper atom and the imine nitrogen atom. The Cu–N(pyridine) bond is still the longest of these three. This is different from all of the other copper(II) complexes of ligands $(L^1)^-$ and $(L^2)^-$ described above and in our recently published paper.[2] The S(apical)–Cu(1)–N(basal) angles range from 92.35(7) to 98.50(7)° while the *cis* basal angles are in the range 80.99(10) to 98.06(11)°. The *cis* basal angles are the same, within experimental error, as they are in the monomeric copper(II) complex [CuL^1Cl], except the N(3)–Cu–N(20) angle [97.38(10)°] which is smaller than the N(3)–Cu–Cl(1) angle [99.59(7)°] in [CuL^1Cl], as might be expected given the greater size of Cl over N.

Table 2. Selected bond lengths [Å] and angles [°] for [$Cu_2(L^1)_2(\mu_{1,3}\text{-}NCS)_2$] (**3**) (symmetry transformations used to generate equivalent atoms: a $-x + 1$, $-y + 1$, $-z + 1$).

Cu(1)–N(1)	1.960(2)	N(2)–Cu(1)–N(20)	167.80(10)
Cu(1)–N(2)	1.950(2)	N(2)–Cu(1)–N(1)	81.82(10)
Cu(1)–N(3)	2.017(2)	N(20)–Cu(1)–N(1)	98.06(11)
Cu(1)–N(20)	1.958(3)	N(2)–Cu(1)–N(3)	80.99(10)
Cu(1)–S(20a)	2.8283(10)	N(20)–Cu(1)–N(3)	97.38(10)
		N(1)–Cu(1)–N(3)	161.65(10)
Cu···Cu(1a)	5.3271(14)	N(2)–Cu(1)–S(20a)	98.50(7)
		N(20)–Cu(1)–S(20a)	93.64(8)
		N(1)–Cu(1)–S(20a)	96.50(7)
		N(3)–Cu(1)–S(20a)	92.35(7)

The two basal planes, formed by N(1), N(2), N(3), N(20) and N(1a), N(2a), N(3a), N(20a), are strictly parallel to each other, by symmetry, and the average distance between the basal planes is 2.913 Å. The four basal atoms are coplanar, with a maximum deviation from the mean basal plane of just 0.037 Å observed for the imine nitrogen atom N(2). The copper atom is located 0.175 Å above the basal plane, towards the apical donor atom.

The double thiocyanate bridges and the two copper(II) atoms form an eight-membered ring, the conformation of which is reminiscent of the chair conformation of cyclohexane, where here it is the two copper atoms which are respectively "up" and "down" (Figure 3), with angles of 93.64° for N(20)–Cu(1)–S(20a) and 89.7° for Cu(1)–S(20a)–C(20a). The mean plane of this eight-membered bridging core forms a dihedral angle of 96.7° with the basal planes, namely, the bridging core mean plane is nearly orthogonal to the two parallel basal planes. This dihedral angle is very similar to that observed in the copper(II) dimers of ligand $(L^2)^-$, [$Cu_2(L^2)_2(\mu\text{-}X)_2$] (X = Cl^-, Br^-, N_3^-). The intramolecular copper–copper separation is 5.3271(14) Å. This is much longer than it is in [$Cu_2(L^2)_2(\mu\text{-}X)_2$] (X = Cl^-, Br^-, N_3^-) [3.3626(4) to 3.7721(27) Å], as expected, due to the end-to-end coordination mode of the bridging thiocyanate. This copper–copper separation is similar to the values reported for related doubly thiocyanate-bridged complexes.[14,17,18]

A π–π interaction is observed between a pyridine ring of one dimer and a pyrrole ring of a neighbouring dimer. The dihedral angle between the mean planes of the two heterocyclic rings, and the angle between the centroid···centroid vector and the normal to the pyridine ring plane, are 11.0° and 38.1°, respectively, whilst the perpendicular distances from each centroid to the other ring are 3.08 and 3.48 Å.

[$Cu(HL^1)Cl_2$] (4) and [$Cu(HL^1)Br_2$] (5)

Blue-green block crystals of [$Cu(HL^1)Cl_2$] and deep green crystals of [$Cu(HL^1)Br_2$] were obtained by the slow diffusion of diethyl ether vapour into an *N*,*N*-dimethylformamide solution of the appropriate complex and the X-ray crystal structures determined (Figure 4, Table 3). This study reveals that [$Cu(HL^1)Cl_2$] is isomorphous with [$Cu(HL^1)Br_2$]. The structures contain monomeric units which are linked together by four hydrogen bonds forming dimers. The coordination geometry at the copper(II) ions is distorted square planar (Σangles at Cu: 371.74° for **4** and 372.07° for **5**). Each is bound to one pyridine nitrogen atom and one imine nitrogen atom of the neutral tridentate ligand HL^1 and to two chloride (**4**) or bromide (**5**) ions, leaving the non-deprotonated pyrrole nitrogen atom uncoordinated. The Cu–N(2) and Cu–N(3) distances in [$Cu(HL^1)Cl_2$] are slightly shorter than those in [$Cu(HL^1)Br_2$]. These distances are longer than those observed in the square-based copper(II) complexes of the ligand $(L^1)^-$, [CuL^1Cl] and [$Cu_2(L^1)_2(\mu_{1,3}\text{-}NCS)_2$]. Cu–N(2) is no longer "short" as N(1) is not bound in **4** and **5**. Consistent with this the Cu–N(2) distance is the same as the Cu–N(3) distance within experimental error, in each structure. The Cu–Cl distances and Cu–Br distances are similar to the reported values for related dichloro[19] and dibromo[20] four-coordinate copper(II) complexes, respectively.

Table 3. Selected bond lengths [Å] and angles [°] for [$Cu(HL^1)X_2$] complexes (X = Cl^-, **4**; X = Br^-, **5**).

	4	**5**
Cu(1)–N(2)	1.975(2)	2.000(4)
Cu(1)–N(3)	1.986(2)	2.008(4)
Cu(1)–X(1)	2.2373(16)	2.3886(7)
Cu(1)–X(2)	2.2257(15)	2.3809(7)
N(2)–Cu(1)–N(3)	82.24(10)	82.09(15)
N(2)–Cu(1)–X(2)	96.96(8)	97.31(10)
N(3)–Cu(1)–X(2)	151.84(7)	151.51(12)
N(2)–Cu(1)–X(1)	153.81(6)	153.58(11)
N(3)–Cu(1)–X(1)	95.93(8)	96.72(12)
X(2)–Cu(1)–X(1)	96.61(6)	95.95(2)

There are two types of hydrogen bonds present (Figure 4). An N–H···X bond (3.259 Å, 162.65° for X = Cl^- and 3.461 Å, 160.77° for X = Br^-) is observed between the pyrrole N–H and one of the coordinated halide ions and a C–H···X bond [3.4120(32) Å, 118.40° for X = Cl^- and

3.5527(43) Å, 118.97° for X = Br^-] is found between the imine C–H [C(6) or C(6a)] and the other coordinated halide ion. The N–H···Cl and C–H···Cl distances in **4** are shorter than N–H···Br and C–H···Br distances, respectively, in **5** as the chloride ion is smaller than the bromide ion. In both cases the N–H···X distance is somewhat shorter than C–H···X distance and this is consistent with the fact that nitrogen is more electronegative than carbon, and hence gives stronger hydrogen bonding.

Magnetochemistry

Variable-temperature magnetic susceptibility measurements were made on $[Cu_2(L^1)_2(\mu_{1,3}\text{-NCS})_2]$ (**3**) in the temperature range 300 to 4 K employing a field of 1 T. The magnetic behaviour is shown in Figure 5 as a plot of both reciprocal molar magnetic susceptibility (χ_M^{-1}) and effective magnetic moment (μ_{eff}) vs. temperature *T*. The raw data from the Squid measurements were corrected for the diamagnetism of the gelatine capsule sample holder, and for the ligand diamagnetic corrections in the usual way. No correction has been made to the χ_M^{-1} and μ_{eff} plots for the temperature-independent paramagnetic susceptibility (60×10^{-6} $cm^3 mol^{-1}$, per Cu).

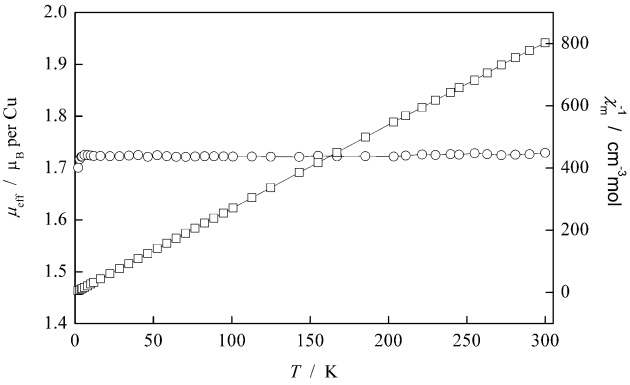

Figure 5. Temperature dependence of the reciprocal magnetic susceptibility, χ_M^{-1} (per Cu) as □, and magnetic moment, μ_{eff} as o, of $[Cu_2(L^1)_2(\mu_{1,3}\text{-NCS})_2]$ (**3**). The solid line is just a guide to the eye.

No intramolecular magnetic interaction was detected between the two copper(II) ions in the end-to-end thiocyanate-bridged square-pyramidal copper(II) dimeric complex, $[Cu_2(L^1)_2(\mu_{1,3}\text{-NCS})_2]$ (**3**). In the temperature range 4–300 K the molar magnetic susceptibility χ_M follows a close to Curie behaviour with best-fit values of the Curie constant, $C = 0.373$ $cm^3 mol^{-1} K$ per Cu; and the Weiss constant, $\theta = -0.23$ K (Figure 5). The room-temperature magnetic moment for **3** is 1.72 BM per copper(II) ion, which is a little lower than the normal range for isolated copper(II) ions (1.9 to 2.2 BM).[21] This indicates that there is no magnetic coupling between the two copper(II) ions which is not unexpected in view of the structure (long NCS bridge and out of plane exchange pathways, Figure 3). A similar result was reported for a closely related doubly thiocyanate-bridged copper(II) complex, α-$[Cu(dmtp)_2(NCS)_2]_2$ (dmtp is 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine).[18] The tiny decrease in μ_{eff} below ca. 3 K (Figure 5) might indicate very weak antiferromagnetic coupling is occurring but is more likely due to Zeeman and thermal depopulation effects.

Conclusions

A series of copper(II) complexes of $(L^1)^-$ in the form of $[CuL^1Cl]$ (**1**), $[CuL^1Br]_n$ (**2**) and $[Cu_2(L^1)_2(\mu_{1,3}\text{-NCS})_2]$ (**3**), and of HL^1 in the form of $[Cu(HL^1)X_2]$ (X = Cl^-, **4**; X = Br^-, **5**), has been prepared and characterised. The weakly acidic pyrrole NH was deprotonated in the presence of triethylamine to facilitate the tridentate coordination of $(L^1)^-$ to the copper(II) ion. The conversion of $[Cu(HL^1)Cl_2]$ (**4**) to $[CuL^1Cl]$ (**1**) has been achieved by first using silver ions to remove one equivalent of chloride ions from the copper(II) complex and then adding one equivalent of triethylamine to deprotonate the pyrrole NH. However, the reverse conversion, from $[CuL^1Cl]$ to $[Cu(HL^1)Cl_2]$, was not successful.

Complexes **1**, **3**, **4** and **5** were characterised by X-ray crystallography. Comparison of crystal structures of the copper(II) complexes of methylene-linked $(L^1)^-$ and ethylene-linked $(L^2)^-$ ligands shows that the more flexible $(L^2)^-$ ligand tends to lead to the formation of dimeric copper(II) complexes while monomeric and dimeric copper(II) complexes of the less flexible ligand $(L^1)^-$ are both possible, depending on the identity of the bridging ligands. Variable-temperature magnetic susceptibility data were recorded for the end-to-end thiocyanate doubly-bridged square-pyramidal copper(II) dimer **3**. Not surprisingly, no intramolecular magnetic coupling was detected between the two copper(II) ions, presumably due to the almost perpendicular arrangement of the magnetic orbitals and the 3-atom bridges, i.e. complex **3** exhibits Curie-like magnetic behaviour.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded with a Varian 500 MHz Inova spectrometer. ^1H and ^{13}C spectra in $CDCl_3$ were referenced to $CHCl_3$ (7.26 ppm) and (77.08 ppm), respectively. Infrared spectra were obtained with a Perkin–Elmer Spectrum BX FT-IR System as pressed KBr discs. MS spectra were collected on a Shimadzu QP8000 alpha with an ESI probe. UV/Vis spectra were obtained with a Varian 500 Scan UV/Vis/NIR spectrophotometer. Molar conductivity measurements were carried out with a Suntex SC-170 conductivity meter. Elemental analyses were carried out by the Campbell Microanalytical Laboratory at the University of Otago. Magnetic data were recorded over the range 300–4.2 K with a Quantum Design MPMS5 SQUID magnetometer with an applied field of 1 Tesla. Where noted, acetonitrile was dried with calcium hydride and distilled. All other chemicals and solvents were of reagent grade and were used as received.

***N*-(1*H*-Pyrrol-2-ylmethylene)(2-pyridinyl)methanamine (HL^1):**[2,4,7] A solution of pyrrole-2-carbaldehyde (1.902 g, 20.0 mmol) in absolute ethanol (30 mL) was added to a solution of 2-(aminomethyl)-pyridine (2.163 g, 20.0 mmol) in absolute ethanol (20 mL). The resulting bright yellow solution was left stirring overnight (24 h).

Evaporation of the solvent in vacuo yielded a yellow oil. The oil was pumped under vacuum overnight and a yellow solid, HL^1, formed (3.6145 g, 98%). $C_{11}H_{11}N_3$ (185.23): calcd. C 71.33, H 5.99, N 22.73; found C 71.17, H 5.94, N 22.73. IR (KBr disc): $\tilde{\nu}_{max}$ = 3128, 3116, 3097, 3076, 2961, 2894, 2845, 1630, 1593, 1567, 1476, 1435, 1420, 1347, 1304, 1131, 1092, 1032, 1016, 1003, 900, 881, 789, 736, 631, 607, 520 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.57 [ddd, J = 4.9, J = 1.8, J = 0.9 Hz, 1 H, pyridine (py)], 8.24 (q, J = 1.1 Hz, 1 H, imine-*CH*=N-), 7.63 (td, J = 7.7, J = 1.9 Hz, 1 H, py), 7.32 (dt, J = 7.8, J = 1.0 Hz, 1 H, py), 7.16 (m, 1 H, py), 6.85 [ddd, J = 2.7, J = 1.4, J = 0.7 Hz, 1 H, pyrrole (pyr)], 6.54 (dd, J = 3.6, J = 1.4 Hz, 1 H, pyr), 6.24 (dd, J = 3.6, J = 2.7 Hz, 1 H, pyr), 4.86 (d, J = 0.8 Hz, 2 H, py-CH_2-) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 159.6 (py), 153.6 (imine-*CH*=N-), 149.4 (py), 136.7 (py), 130.2 (pyr), 122.2 (py), 122.02 (py), 121.98 (pyr), 114.8 (pyr), 109.9 (pyr), 66.3 (py-CH_2-) ppm. ES-MS: m/z = 186 $[M + H]^+$.

$[CuL^1Cl]$ (1). Method (a): Ligand HL^1 (0.0741 g, 0.400 mmol) was dissolved in methanol (3 mL) and triethylamine (0.0405 g, 0.400 mmol) in methanol (2 mL) added. This solution was added dropwise to an apple-green solution of copper(II) chloride dihydrate (0.0682 g, 0.400 mmol) in methanol (5 mL), over which time a precipitate formed and the solution colour changed to green yellow. The resulting mixture was stirred for 6 h after which the dark green solid was collected by filtration, washed with methanol and dried in vacuo (0.0810 g, 72%). $C_{11}H_{10}ClCuN_3$ (283.21): calcd. C 46.65, H 3.56, N 14.84, Cl 12.52; found C 46.71, H 3.57, N 14.62, Cl 12.55. IR (KBr disc): $\tilde{\nu}_{max}$ = 3104, 3089, 3063, 3029, 2903, 2883, 2820, 1609, 1589, 1561, 1479, 1445, 1389, 1305, 1282, 1087, 1032, 742 cm^{-1}. ES-MS: m/z = 531 $[Cu_2(L^1)_2Cl]^+$, 432 $[Cu(L^1)_2]^+$, 288 $[CuL^1(CH_3CN)]^+$, 247 $[CuL^1]^+$. UV (MeOH): λ_{max} (ε/$dm^3\,mol^{-1}\,cm^{-1}$) = 250 (1.14×10^4), 293 (7.4×10^3), 367 (1.27×10^4), 617 (257) nm.

Method b. Conversion of $[Cu(HL^1)Cl_2]$ into $[CuL^1Cl]$: One equivalent of silver tetrafluoroborate (0.0584 g, 0.300 mmol) in methanol (10 mL) was added to a bright green solution of $[Cu(HL^1)Cl_2]$ (0.0959 g, 0.3 mmol) in methanol (120 mL) followed by triethylamine (0.0304 g, 0.300 mmol) in methanol (10 mL). The resulting cloudy blue solution was stirred for 6 h. The solid, silver chloride, was then filtered off with a frit (no. 4) containing Celite and the dark green filtrate was rotary-evaporated to dryness. The residue was taken up in acetonitrile (5 mL) and the desired dark green product, $[CuL^1Cl]$, was filtered off, washed with acetonitrile and dried in vacuo (0.0469 g, 55%). $C_{11}H_{10}ClCuN_3$ (283.22): calcd. C 46.65, H 3.56, N 14.84, Cl 12.52; found C 46.53, H 3.37, N 14.92, Cl 12.07. IR (KBr disc): $\tilde{\nu}_{max}$ = 3104, 2924, 2883, 2853, 1609, 1589, 1561, 1445, 1389, 1305, 1282, 1032, 741 cm^{-1}.

$[CuL^1Br]_n$ (2): Ligand HL^1 (0.0741 g, 0.400 mmol) was dissolved in methanol (10 mL) and triethylamine (0.0405 g, 0.400 mmol) in methanol (2 mL) added. To this solution was added dropwise a deep yellow solution of copper(II) bromide (0.0893 g, 0.400 mmol) in methanol (10 mL), over which time a precipitate formed. The resulting mixture was stirred for 8 h after which the olive green solid was filtered off, washed with methanol and dried in vacuo (0.0845 g, 65%). $[C_{11}H_{10}N_3CuBr]_n$ $(327.67)_n$: calcd. C 40.32, H 3.08, N 12.82, Br 24.39; found C 40.43, H 3.13, N 12.72, Br 24.09. IR (KBr disc): $\tilde{\nu}_{max}$ = 3102, 3083, 3062, 2898, 2880, 1609, 1587, 1561, 1479, 1444, 1390, 1304, 1282, 1033, 741. ES-MS: m/z = 288 $[CuL^1(CH_3CN)]^+$, 247 $[CuL^1]^+$. UV (MeOH): λ_{max} (ε/$dm^3\,mol^{-1}\,cm^{-1}$) = 249 (1.04×10^4), 290 (6.03×10^3), 368 (1.15×10^4), 430 (shoulder, 1.82×10^3), 610 (242) nm.

$[Cu_2(L^1)_2(\mu_{1,3}\text{-}NCS)_2]$ (3): HL^1 (0.0741 g, 0.400 mmol) was dissolved in methanol (3 mL) and triethylamine (0.0405 g, 0.4 mmol) in methanol (2 mL) was added. The resulting solution was added dropwise to a pale blue solution of copper(II) tetrafluoroborate tetrahydrate (0.1237 g, 0.400 mmol) in methanol (4 mL), leading to a deep green solution. Sodium thiocyanate (0.0324 g, 0.4 mmol) in methanol (3 mL) was then added and after stirring for around 5 min a precipitate formed. The resulting mixture was stirred for 8 h after which the deep blue solid was filtered off, washed with methanol and dried in vacuo (0.0932 g, 76%). $C_{22}H_{20}N_6Cu_2(NCS)_2$ (611.68): calcd. C 47.13, H 3.30, N 18.32, S 10.48; found C 46.67, H 3.06, N 18.60, S 10.68. IR (KBr disc): $\tilde{\nu}_{max}$ = 3093, 2999, 2922, 2885, 2095, 1608, 1595, 1561, 1441, 1387, 1301, 1280, 1031, 750 cm^{-1}. ES-MS: m/z = 554 $[Cu_2(L^1)_2(NCS)]^+$, 432 $[Cu(L^1)_2]^+$, 247 $[CuL^1]^+$. UV (MeOH): λ_{max} [ε (per Cu^{2+})/$dm^3\,mol^{-1}\,cm^{-1}$] = 244 (8.67×10^3), 293 (4.6×10^3), 369 (9.0×10^3), 433 (shoulder, 918), 618 (133) nm.

$[Cu(HL^1)Cl_2]$ (4): A solution of HL^1 (0.1389 g, 0.750 mmol) in methanol (5 mL) was added dropwise to an apple green solution of copper(II) chloride dihydrate (0.1278 g, 0.750 mmol) in methanol (10 mL) over which time a green precipitate formed and the solution changed to dark green. The resulting mixture was stirred for 3.5 h after which the green solid was collected by filtration, washed with methanol and dried in vacuo (0.1939 g, 81%). $C_{11}H_{11}N_3CuCl_2$ (319.67): calcd. C 41.33, H 3.47, N 13.18, Cl 22.18; found C 41.54, H 3.13, N 13.18, Cl 22.16. IR (KBr disc): $\tilde{\nu}_{max}$ = 3240, 3128, 3106, 3072, 2995, 2957, 2917, 1621, 1571, 1488, 1427, 1378, 1286, 1146, 1036, 760 cm^{-1}. ES-MS: m/z = 603 $[Cu_2(HL^1)_2Cl_3]^+$, 283 $[Cu(HL^1)Cl]^+$, 288 $[CuL^1(CH_3CN)]^+$, 247 $[Cu(HL^1) - H]^+$. $\Lambda_m/\Omega^{-1}\,cm^2\,mol^{-1}$: 64 in methanol (cf. 80 to 115 for a 1:1 electrolyte in methanol[22]) and 14 in DMF (cf. 65 to 90 for a 1:1 electrolyte in DMF[22]). UV (MeOH): λ_{max} (ε/$dm^3\,mol^{-1}\,cm^{-1}$) = 255 (9.16×10^3), 309 (1.39×10^4), 367 (9.0×10^3), 709 (94) nm.

$[Cu(HL^1)Br_2]$ (5): A solution of HL^1 (0.0741 g, 0.400 mmol) was added dropwise to a deep yellow solution of copper(II) bromide (0.0893 g, 0.400 mmol) in methanol over which time a dark green precipitate formed. The resulting mixture was stirred for 7 h after which the solid was filtered off, washed with methanol and dried in vacuo (0.1266 g, 77%). $C_{11}H_{11}Br_2CuN_3$ (408.59): calcd. C 32.34, H 2.71, N 10.28, Br 39.11; found C 32.55, H 2.55, N 10.27, Br 39.21. IR (KBr disc): $\tilde{\nu}_{max}$ = 3266, 3128, 3102, 2911, 1618, 1570, 1488, 1447, 1425, 1359, 1286, 1141, 1035, 758 cm^{-1}. ES-MS: m/z = 737 $[Cu_2(HL^1)_2Br_3]^+$, 329 $[Cu(HL^1)Br]^+$, 288 $[CuL^1(CH_3CN)]^+$, 186 $[HL^1 + H]^+$. $\Lambda_m/\Omega^{-1}\,cm^2\,mol^{-1}$: 77 in methanol (cf. 80 to 115 for a 1:1 electrolyte in methanol[22]) and 43 in DMF (cf. 65 to 90 for a 1:1 electrolyte in DMF[22]). UV (MeOH): λ_{max} (ε/$dm^3\,mol^{-1}\,cm^{-1}$) = 250 (1.03×10^4), 304 (9.77×10^3), 367 (1.12×10^4), 710 (138).

X-ray (Crystallography): All data were collected with a Bruker SMART diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarisation effects and semi-empirical absorption corrections (SADABS) were applied. The structures were all solved by direct methods except for $[Cu(HL^1)Cl_2]$ which was solved by the Patterson method (SHELXS-97),[23] and refined against F^2 using all data by full-matrix least-squares techniques (SHELXL-97).[23] All non-hydrogen atoms were made anisotropic. Hydrogen atoms were inserted at calculated positions and rode on the atoms to which they are attached (including their isotropic thermal parameters which were equal to 1.2 times the equivalent isotropic displacement parameter for the attached non-hydrogen atom) except the hydrogen atom on N1 in $[Cu(HL^1)Cl_2]$ and in $[Cu(HL^1)Br_2]$ where this hydrogen atom was instead located from a difference map and fixed. A summary of the crystallographic data and refinement parameters is given in Table 4.

Table 4. Details of the crystal-structure determination for complexes **1**, **3**, **4** and **5**.

	1	**3**	**4**	**5**
Empirical formula	$C_{11}H_{10}ClCuN_3$	$C_{24}H_{20}Cu_2N_8S_2$	$C_{11}H_{11}Cl_2CuN_3$	$C_{11}H_{11}Br_2CuN_3$
Formula mass	283.21	611.68	319.67	408.59
Temperature/K	168(2)	168(2)/K	168(2)	200(2)
Crystal system	monoclinic	orthorhombic	triclinic	triclinic
Space group	$P2_1/c$	$Pbca$	$P\bar{1}$	$P\bar{1}$
a [Å]	7.344(4)	16.474(5)	7.680(6)	7.80870(10)
b [Å]	7.995(2)	8.512(2)	8.129(6)	8.44340(10)
c [Å]	18.667(5)	17.573(5)	11.299(9)	11.5676(2)
α [°]	90	90	617.3(9)	78.9970(10)
β [°]	95.269(3)	90	78.749(10)	79.4840(10)
γ [°]	90	90	79.943(11)	63.6480(10)
V [Å^3]	1091.5(7)	2464.2(12)	63.73(2)	666.699(16)
Z	4	4	2	2
$\rho_{calcd.}$ [g/cm^3]	1.723	1.649	1.720	2.035
μ [mm^{-1}]	2.217	1.927	2.180	7.611
$F(000)$	572	1240	322	394
Crystal size [mm]	0.45 × 0.20 × 0.06	0.68 × 0.25 × 0.06	0.35 × 0.27 × 0.17	0.36 × 0.26 × 0.20
θ range for data collection [°]	2.19–26.38	2.32–26.46	2.82–26.42	1.80–27.58
Reflections collected	13631	21433	8162	6400
Independent reflections	2212	2507	2505	2712
R(int)	0.0321	0.0338	0.0172	0.1124
Max./min. transmission	1.00/0.72	1.00/0.83	1.00/0.90	0.3113/0.1703
Data/restraints/parameters	2212/0/145	2507/0/163	2505/0/158	2712/0/158
Goof (F^2)	1.148	1.134	1.069	1.066
R_1 [$I > 2\sigma(I)$]	0.0319	0.0386	0.0277	0.0454
wR_2 (all data)	0.0719	0.0878	0.0681	0.1266

CCDC-722517 (for **1**), -722518 (for **3**), -722519 (for **4**), -722520 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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