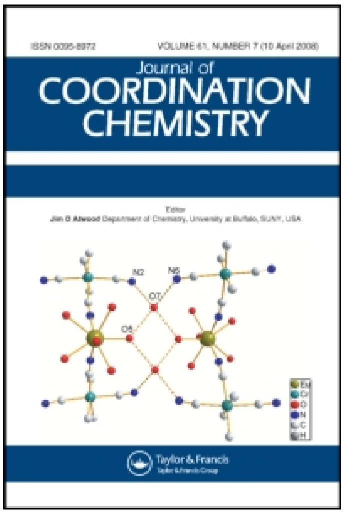

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Complexes of a New N_3S_2 Macrocycle: Synthesis, Structure and Electrospray Mass Spectrometry

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COMPLEXES OF A NEW N_3S_2 MACROCYCLE: SYNTHESIS, STRUCTURE AND ELECTROSPRAY MASS SPECTROMETRY

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The silver(I) complex of a 15-membered macrocyclic ligand with an N_3S_2 donor set (L^1) has been prepared by the reaction of 2,6-diacetylpyridine with 1,8-diamino-3,6-dithiaoctane in the presence of silver(I) ions. A reduced form (L^2) of the ligand, in which the imine groups are converted to amines, was prepared by the reduction of the silver(I) complex by sodium borohydride. The ligand L^2 has been characterised by various spectroscopic techniques and the copper(II) complex has been prepared. The metal complexes of L^1 and L^2 have been characterised by electrospray mass spectrometry and UV-visible spectroscopy. The copper(II) complex of L^1 has been synthesised from $[AgL^1]^+$ via metal exchange. $[CuL^1](ClO_4)_2$ crystallises in the orthorhombic space group $Pna2_1$ with $a = 14.374(5)$ Å, $b = 12.947(3)$ Å, $c = 11.824(3)$ Å with $Z = 4$. The geometry about the metal centre approximates trigonal bipyramidal with the pyridinyl nitrogen and the sulfur donors in the equatorial positions and the imine nitrogen donors in the axial positions. Metal ion exchange and the relative stabilities of metal complexes of the macrocyclic ligands were studied by electrospray mass spectrometry.

Keywords: N_3S_2 Macrocycles; Structure; Electrospray mass spectrometry

INTRODUCTION

There has been strong recent interest in the complexation properties of nitrogen-containing macrocycles used as ligands for metal ions [1–3]. Studying the relative stabilities of the metal complexes is of great interest in attempting to develop ligands with high formation constants for complexes with specific metal ions [4]. Many macrocyclic ligands have been synthesised by reacting 2,6-diacetylpyridine with a variety of α,ω-diamines [5,6]. In these reactions 2,6-diacetylpyridine may react with the diamine in a 1:1 mole ratio $(1+1)$ or, if two molecules of each reagent react in a concerted manner $(2+2)$, a larger macrocycle will be synthesised with a consequent

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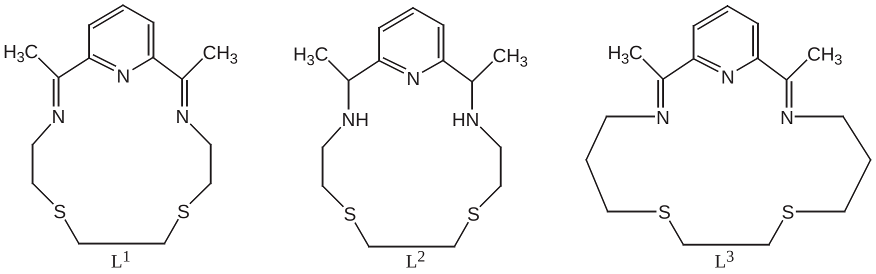
greater number of donor atoms. The composition of the product, either $(1+1)$ or $(2+2)$, depends on the nature of the reactants and on the template metal cation. Previously, the versatile co-ordination properties of a 17-membered macrocycle, 2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo[14.3.1]icosa-1(20),2,14,16,18-pentane (L^3), have been studied [7]. Complexes of L^3 with Ag^I, Cu^I and Cu^{II} have been prepared and their structures determined. Here we report new macrocyclic complexes of 15-membered ligands L^1 and L^2 both containing an N_3S_2 donor set. Ligand L^1 was prepared by a silver(I)-templated Schiff-base condensation and the Cu^I and Cu^{II} complexes were available via metal exchange with $[AgL^1](ClO_4)$. The structure of the copper(II) complex, $[CuL^1](ClO_4)_2$, has been determined using X-ray diffractometry. Mass spectrometry has been used to characterise the complexes, to assess the selectivity of a particular ligand system and to study the relative stability constants for the complexes with a number of metal ions.



SCHEME 1

EXPERIMENTAL

Instrumentation

UV-Vis spectra were recorded with a Shimadzu UV2101PC spectrophotometer. The IR spectra were recorded on a FT-IR Nicolet Magna IR-760 spectrometer with compounds dispersed in KBr discs (for the complexes) or sandwiched between NaCl plates (for the ligand L^2). Elemental microanalyses was performed by the Microanalytical Unit, Research School of Chemistry, Australian National University. The NMR spectra were recorded on a Bruker Advance DPX300 spectrometer in $(CD_3)_3SO$ solution, using solvent as an internal standard. Electrospray mass spectrometry (ES-MS) was carried out on a Perkin-Elmer SCIEX API300 Triple Quadrupole LC/MS/MS Mass Spectrometer with liquid chromatography accessories. The general conditions for ES-MS were: ion spray voltage = 5000 V, drying gas temperature = 50°C, orifice voltage = 30 V, ring voltage = 340 V, and syringe pump injection (e.g., flow rate = $5\,\mu L\,min^{-1}$). Spectra were averaged over 10–15 scans. The m/z values quoted represent the most abundant peak in the ion cluster.

Synthesis

2,6-Diacetylpyridine (Aldrich) was used as supplied and 1,8-diamino-3,6-dithiaoctane was prepared by the method of Hay *et al.* [8].

$[AgL^1](ClO_4)\cdot H_2O$

The complex was synthesised by a modification of the literature method for L^3 [7]. To a solution of $AgNO_3$ (0.02 mol) in methanol (400 mL), 2,6-diacetylpyridine (0.02 mol) in methanol (50 mL) was added with stirring. A solution of 1,8-diamino-3,6-dithiaoctane (0.02 mol) in methanol (50 mL) was added to this light-yellow solution. The mixture was heated under reflux for 16 h, the yellow colour intensified and black silver metal separated. The hot solution was filtered into a methanolic solution of $NaClO_4{\cdot}H_2O$ (6 g in 50 mL). The yellow crystals of product separated on cooling in 60% yield. ES mass spectrum: *m*/*z* 414.0 ($[^{107}AgL^1]^+$). IR (KBr disc): 1632 (C=N), 1400–1580 (pyridyl), 1080, 628 cm^{-1} (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$]: δ 8.26–8.34 (pyridine), δ 3.12–3.70(CH_2) and δ 2.52–2.54 ppm (CH_3). ^{13}C NMR [$(CD_3)_2SO$]: δ 124.60–150.10 (pyridine), δ 167.82 (C=N), δ 16.28 (CH_3) and δ 34.15–47.02 ppm (CH_2). Anal. Cald. for $C_{15}H_{21}N_3S_2ClO_4Ag\cdot H_2O$(%): C, 33.80; H, 4.31; N, 7.88. Found: C, 33.32; H, 3.94; N, 7.55.

$[CuL^1](ClO_4)_2\cdot H_2O$

A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.02 mol) in methanol (20 mL) was added to a solution of $[AgL^1][ClO_4]$ (0.02 mol) in methanol (150 mL). The colour changed from yellow to deep blue immediately and a blue powder separated. The product was recrystallised by vapour diffusion of diethyl ether into an acetonitrile solution. ES mass spectrum: *m*/*z* 370.2 ($[^{63}CuL^1]^+$). IR (KBr disc): 1640 (C=N), 1400–1580 (pyridyl), 1080, 628 cm^{-1} (ClO_4^-). Anal. Cald. for $C_{15}H_{21}N_3S_2Cl_2O_8Cu\cdot H_2O$(%): C, 30.82; H, 3.94; N, 7.19. Found: C, 30.61; H, 4.10; N, 7.13.

$[CuL^1](ClO_4)$

To a hot solution of $[CuL^1](ClO_4)_2$ (0.0002 mol) in methanol–acetonitrile (100 mL), $Na[BH_4]$ (0.0002 mol) in methanol (20 mL) was added. The colour changed from blue to brown. The filtrate was concentrated to yield brown plates in 50% yield. ES mass spectrum: *m*/*z* 370.2 ($[^{63}CuL^1]^+$). IR (KBr disc): 1635 (C=N), 1400–1580 (pyridyl), 1080, 624 cm^{-1} (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$]: δ 8.17–8.20 (pyridine), δ 2.44–3.16 (CH_2) and δ 1.21 ppm (CH_3). ^{13}C NMR [$(CD_3)_2SO$]: δ 120.47–139.40 (pyridine), δ 152 (C=N), δ 21.84 (CH_3) and δ 28.40–47.65(CH_2). Anal.: Cald. for $C_{15}H_{21}N_3S_2ClO_4Cu$(%): C, 38.29; H, 4.50; N, 8.93. Found: C, 38.02; H, 4.52; N, 9.12.

L^2

An excess of $Na[BH_4]$ was added to a refluxing methanol solution of $[AgL^1](ClO_4)$. The precipitated silver metal was removed by filtration and the filtrate evaporated to dryness. A concentrated solution of NaOH in water (5 g in 10 mL) was added and the liberated L^2 was extracted into chloroform. Rotary evaporation yielded L^2 as a brown oil. ES mass spectrum: *m*/*z* 312.0 (L^2H^+). IR (NaCl plate): 3240, 1605 (N–H), 1400–1580 cm^{-1} (pyridyl). ^{1}H NMR [$(CD_3)_2SO$]: δ 7.60-7.96 (pyridine), δ 2.50–3.37 (CH_2), δ 3.15 (CH) and δ 1.78–1.81 ppm (CH_3). ^{13}C NMR [$(CD_3)_2SO$]: δ 140–167 (pyridine), δ 24.10 (CH_3), δ 34.01 (CH) and δ 28.50–47.0 ppm (CH_2). Anal. Cald. for $C_{15}H_{25}N_3S_2$.½ $CHCl_3$(%): C, 50.13; H, 7.00; N, 11.32. Found C, 49.89; H, 7.14; N, 11.41.

$[CuL^2](ClO_4)_2$

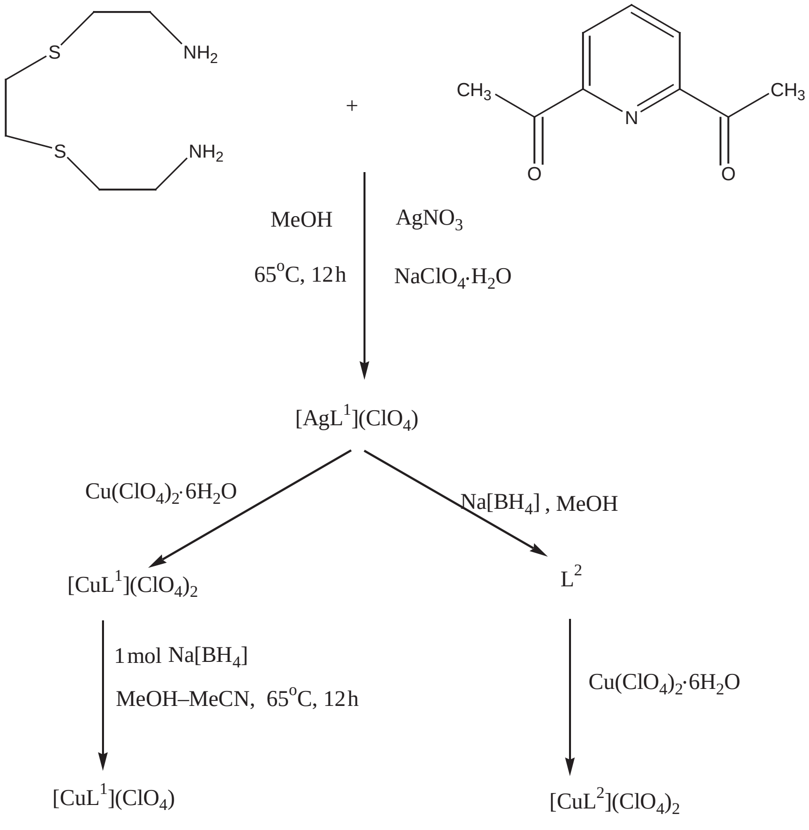
To a hot solution of L^2 (0.02 mol) in methanol (50 mL) was added a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.02 mol) in methanol (100 mL). The resulting deep-blue solution was refluxed for 15 min, filtered hot, and allowed to concentrate slowly. A microcrystalline blue solid was separated and washed with cold ethanol. ES mass spectrum: m/z 373.0 ($[^{63}CuL^2–H]^+$). IR (KBr disc): 3220, 1600 (N–H) 1400–1550 (pyridyl), 1085, 625 cm^{-1} (ClO_4^-). Anal. Cald. for $C_{15}H_{25}N_3S_2Cl_2O_8Cu$(%): C, 31.39; H, 4.39; N, 7.32. Found: C, 31.33; H, 4.24; N, 7.09.

RESULTS AND DISCUSSION

Synthesis

The syntheses of the macrocyclic ligands and complexes studied are summarised in Scheme 2.

The silver(I) complex was prepared by the template action of silver(I) ions to effect a 1 + 1 cyclic Schiff-base condensation of 2,6-diacetylpyridine with 1,8-diamino-3,6-dithiaoctane in methanol. In the absence of silver(I) ions, cyclisation was unsuccessful, demonstrating the template effect of the metal ions. Treatment of $[AgL^1]ClO_4$ with an



SCHEME 2

excess of $Cu(ClO_4)_2 \cdot 6H_2O$ in hot methanol quickly generated a deep-blue solution from which crystals of the copper(II) complex $[CuL^1](ClO_4)_2$ were obtained. Treatment of $[CuL^1](ClO_4)_2$ with one equivalent of $NaBH_4$ under reflux in methanol afforded the copper(I) complex $[CuL^1](ClO_4)$.

Tetrahydroborate reduction of $[AgL^1]ClO_4$ yields the free reduced macrocycle (L^2) where the imino linkages are reduced to secondary amines, thus making available another new macrocyclic ligand.

The analytical data (elemental analyses, ES-MS, IR, ^{1}H and ^{13}C NMR spectra) are consistent with the formulation of the ligands and complexes. Infrared spectra for the complexes $[ML^1](ClO_4)_n$ [$M = Cu^I, n = 1$; Cu^{II}, $n = 2$; and Ag^I, $n = 1$) indicate the presence of the imino (C=N) and pyridinyl group with absorption bands at *ca.* 1620 and 1400–1580 cm^{-1}, respectively. The ν(C=N) mode is absent in the spectra of the reduced ligand L^2 and the complex $[CuL^2](ClO_4)_2$; instead, the spectra show single bands at 3250 cm^{-1} and at 1600–1605 cm^{-1} attributable to the stretching and bending vibrations of the secondary NH group. The ^{1}H and ^{13}C NMR spectra of the diamagnetic complexes $[AgL^1]ClO_4$ and $[CuL^1]ClO_4$ both consist of well resolved peaks that are interpretable in terms of the ligand structure. The ^{1}H and ^{13}C NMR spectra of the reduced ligand L^2 are consistent with the proposed structure.

Crystal Structure

The complex of $[CuL^1](ClO_4)_2$ was recrystallised by slow evaporation of the solvent to yield X-ray-quality crystals. A summary of crystal data and refinement results for the complex is shown in Table I. An ORTEP-II representation, with labelling scheme, of the cation of the copper(II) complex is shown in Fig. 1, metal–donor atom bond lengths, selected angles and atomic coordinates and displacement parameters are presented in Tables II–IV.

TABLE I Summary of crystal data and refinement results for the complex

Empirical formula	$C_{15}H_{21}Cl_2CuN_3O_8S_2$
Formula weight	$M = 569.9$
Crystal system	Orthorhombic
Space group	$Pna2_1$
a (Å)	14.374(5)
b (Å)	12.947(3)
c (Å)	11.824(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2200(1)
Z	4
T (K)	294
D_{calcd} (g cm^{-3})	1.72
$F(000)$	1164
2θ max (°)	50.00
Range of h, k, l	$0 \sim 17, 0 \sim 15, 0 \sim 14$
No. of reflections collected	2025
No. of independent reflections	1226
$R(I > 3\sigma(I))$ on F	0.042
$wR(I > 3\sigma(I))$ on F	0.055
Goodness-of-fit	1.91
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.74, − 1.12

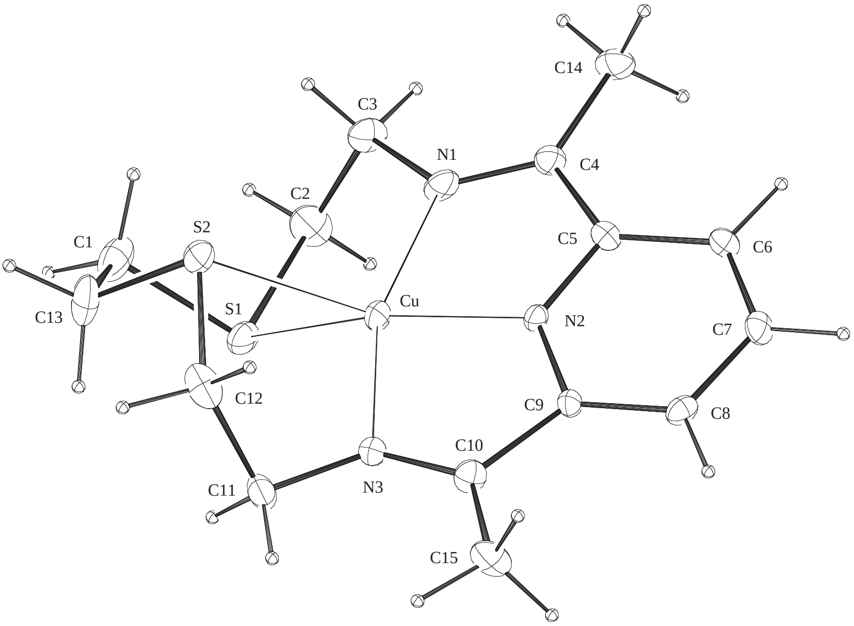


FIGURE 1 View of the $[CuL^1]^{2+}$ cation, showing the atom numbering.

TABLE II Bond lengths (Å) for the cation of $[CuL^1][ClO_4]_2$

Cu–N(1)	1.983(11)	N(3)–C(10)	1.300(14)
Cu–N(2)	1.907(9)	N(3)–C(11)	1.439(17)
Cu–N(3)	2.018(10)	C(1)–C(13)	1.476(25)
Cu–S(1)	2.397(3)	C(2)–C(3)	1.426(21)
Cu–S(2)	2.570(4)	C(4)–C(5)	1.437(17)
S(1)–C(1)	1.833(17)	C(4)–C(14)	1.475(18)
S(1)–C(2)	1.816(19)	C(5)–C(6)	1.416(16)
S(2)–C(12)	1.850(18)	C(6)–C(7)	1.326(17)
S(2)–C(13)	1.860(20)	C(7)–C(8)	1.405(18)
N(1)–C(3)	1.460(15)	C(8)–C(9)	1.351(14)
N(1)–C(4)	1.302(16)	C(9)–C(10)	1.497(19)
N(2)–C(5)	1.322(15)	C(10)–C(15)	1.459(17)
N(2)–C(9)	1.356(14)	C(11)–C(12)	1.577(21)

TABLE III Selected bond angles (°) for $[CuL^1][ClO_4]_2$

N(1)–Cu–N(2)	78.9(5)	S(1)–Cu–N(2)	146.7(3)
N(1)–Cu–N(3)	159.5(4)	S(1)–Cu–N(3)	111.9(3)
N(2)–Cu–N(3)	80.6(4)	S(2)–Cu–N(1)	112.8(3)
S(1)–Cu–S(2)	85.1(1)	S(2)–Cu–N(2)	128.1(3)
S(1)–Cu–N(1)	85.3(4)	S(2)–Cu–N(3)	81.0(3)

The X-ray data were collected on an Enraf-Nonius CAD4 diffractometer operating in θ–2θ scan mode using graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods and refined by the method of least-squares [9]. ORTEP-II [10] was used for the structural diagrams including thermal ellipsoids.

The metal centre is bound to all five potential donor atoms of the macrocycle with the copper atom lying in the N_3 plane (defined by the pyridinyl nitrogen atom and

TABLE IV Atomic coordinates and displacement parameters for non-hydrogen atoms in $[CuL^1][ClO_4]_2$ Esd in parentheses.

Atom	*x*	y	*z*	U_{eq}
Cu	0.2764(1)	0.5557(1)	0.2500	0.0524(4)
S(1)	0.1645(2)	0.4187(2)	0.2582(4)	0.0672(9)
S(2)	0.1694(3)	0.6475(3)	0.3923(4)	0.071(1)
N(1)	0.2346(7)	0.5729(8)	0.0913(10)	0.065(3)
N(2)	0.3869(6)	0.6073(6)	0.1809(9)	0.043(2)
N(3)	0.3615(6)	0.5553(7)	0.3858(9)	0.056(3)
C(1)	0.0637(10)	0.4827(11)	0.3221(19)	0.097(6)
C(2)	0.1344(11)	0.4299(15)	0.1095(17)	0.105(6)
C(3)	0.1441(9)	0.5301(11)	0.0606(13)	0.073(5)
C(4)	0.2948(9)	0.6140(11)	0.0224(11)	0.058(4)
C(5)	0.3836(8)	0.6349(8)	0.0733(10)	0.047(3)
C(6)	0.4678(9)	0.6684(9)	0.0229(10)	0.052(3)
C(7)	0.5446(9)	0.6727(9)	0.0849(13)	0.058(3)
C(8)	0.5450(7)	0.6483(8)	0.2006(11)	0.053(3)
C(9)	0.4644(6)	0.6143(7)	0.2460(12)	0.045(2)
C(10)	0.4454(9)	0.5887(10)	0.3673(11)	0.059(3)
C(11)	0.3213(10)	0.5463(11)	0.4968(12)	0.071(4)
C(12)	0.2539(13)	0.6415(11)	0.5102(14)	0.083(5)
C(13)	0.0925(13)	0.5363(16)	0.4265(16)	0.111(6)
C(14)	0.2787(10)	0.6388(11)	−0.0978(12)	0.074(4)
C(15)	0.5185(11)	0.6098(11)	0.4498(12)	0.079(5)
ClA	0.3236(7)	0.8790(7)	0.2494(9)	0.072(6)
O1A	0.3535(12)	0.9791(10)	0.2176(19)	0.126(6)
O2A	0.4000(11)	0.8226(12)	0.2932(16)	0.133(9)
O3A	0.2873(12)	0.8271(16)	0.1536(14)	0.109(8)
O4A	0.2536(11)	0.8871(15)	0.3332(14)	0.141(9)
ClA′	0.3325(9)	0.8721(9)	0.2256(13)	0.072(5)
O1A′	0.3012(14)	0.9757(11)	0.2306(25)	0.109(8)
O2A′	0.2632(15)	0.8098(19)	0.1748(25)	0.120(8)
O3A′	0.3506(20)	0.8359(21)	0.3365(17)	0.140(9)
O4A′	0.4151(13)	0.8670(19)	0.1606(21)	0.1446(6)
ClB	0.4199(8)	0.3076(9)	0.2276(8)	0.055(6)
O1B	0.3584(13)	0.3588(16)	0.1527(14)	0.079(6)
O2B	0.5051(12)	0.3623(17)	0.2327(17)	0.084(5)
O3B	0.4364(16)	0.2060(10)	0.1880(18)	0.096(9)
O4B	0.3797(13)	0.3034(18)	0.3368(9)	0.096(9)
ClB′	0.4368(12)	0.2910(12)	0.2227(12)	0.057(6)
O1B′	0.5094(18)	0.3630(24)	0.2410(25)	0.089(6)
O2B′	0.4642(22)	0.2194(20)	0.1385(20)	0.101(9)
O3B′	0.3559(17)	0.3439(21)	0.1865(23)	0.075(6)
O4B′	0.4178(20)	0.2377(22)	0.3246(16)	0.098(9)

two imino nitrogen atoms). The two sulfur donors are above and below the CuN_3 plane with the overall geometry being distorted trigonal bipyramidal. In an overall sense, the structure is similar to that of the Cu^{II} and Cu^{I} complexes of the 17-membered N_3S_2 donor macrocycle (L^3) which both have distorted trigonal bipyramidal geometries.

In terms of structural details, the Cu–N(2) (i.e., pyridinyl nitrogen) bond is considerably shorter than either the Cu–N(1) or Cu–N(3) bond. This difference may be due to the different chemical environments of the nitrogen donor atoms or may be yet another example in which $M–N_{central}$ bonds are found to be shorter than $M–N_{distal}$ bonds for complexes of relatively rigid tridentate ligands [11]. In comparison with the structures of the L^3 complexes, presented in Table V, the Cu–N(2) bond length in $[CuL^1]^{2+}$ is the shortest by a considerable margin, with the Cu–N (pyridinyl nitrogen) bond lengths in $[CuL^3]^{2+}$ and in $[CuL^3]^{+}$ being 1.930(11) and 2.103(17) Å, respectively, as may be

TABLE V Structural parameters for copper complexes of N_3S_2 macrocyclic ligands

Parameter	$[CuL^1]^{2+}$	$[CuL^3]^{+}$	$[CuL^3]^{2+}$
Cu–$N_{pyridyl}$	1.907(9)	2.103(17)	1.930(11)
Cu–N_{imino}	2.018(10), 1.983(11)	2.519(25), 2.279(22)	2.022(11), 2.079(13)
Cu–S	2.397(3), 2.570(4)	2.328(7), 2.324(8)	2.470(4), 2.377(4)

expected for the difference in oxidation state. The Cu–N(1) and Cu–N(3) bond lengths in $[CuL^1]^{2+}$ are shorter than the Cu–imino nitrogen bonds in $[CuL^3]^{2+}$ (2.022(11), 2.079(13) Å) and in $[CuL^3]^{+}$ (2.519(25) and 2.279(22) Å). In comparing the Cu^{II} structures, the metal–donor atom bonds in the Cu^{II} complex of the 15-membered macrocycle (L^1) are relatively short, possibly simply because the macrocycle is smaller than the 17-membered macrocycle (L^3).

For $[CuL^1]^{2+}$ the two Cu–S bonds are quite long and rather asymmetric with bond lengths of 2.397(3) Å (Cu–S(1)) and 2.570(4) Å (Cu–S(2)). In $[CuL^3]^{+}$, the Cu–S bonds are considerably shorter (2.324(8) and 2.328(7) Å) and identical in length, taking account of experimental error. In $[CuL^1]^{2+}$ the Cu–S bond lengths fall between the values observed for $[CuL^3]^{2+}$ and $[CuL^3]^{+}$ and there is considerable dissimilarity in the values. This suggests that in the Cu^{II} complexes, optimising the interaction with the nitrogen donor atoms gives rise to a [4 + 1] coordination arrangement in which the Cu–S interactions are relatively weak. In the Cu^{I} complex the Cu–S interactions dominate, with the Cu^{I}–S bond being relatively strong and the Cu^{I}–N bonds being quite long. This observation is presumably a manifestation of the different acid–base properties of copper in its two common oxidation states, under the HSAB theory.

Electronic Spectra

The diffuse reflectance spectrum of $[CuL^1](ClO_4)_2$ displayed a broad band which appears around 14300–17900 cm^{-1} (700–560 nm). The diffuse reflectance spectrum of $[CuL^2](ClO_4)_2$ displayed a similar broad band around 15400–17900 cm^{-1} (650–560 nm). The absorption bands within the range 12 500–18 500 cm^{-1} (800–540 nm) correspond to the d–d transitions and suggest that the coordination spheres have distorted trigonal bipyramidal geometry in $[CuL^1](ClO_4)_2$ and $[CuL^2](ClO_4)_2 \cdot [CuL^1](ClO_4)_2$ and $[CuL^2](ClO_4)_2$ in acetonitrile solution showed similar absorption bands around 15 900 cm^{-1} (630 nm) and 17 900 cm^{-1} (560 nm) respectively as in the solid state, indicating that the trigonal bipyramidal coordination is maintained in solution. The spectra of the $[AgL^1](ClO_4)$ complex in both the solid state and acetonitrile solution show a single band near 28 600 cm^{-1} (350 nm) which is assigned to a metal-to-ligand charge transfer transition. The $[CuL^1](ClO_4)$ complex in acetonitrile solution exhibits a strong band at 22 700 cm^{-1} (440 nm) which we assume is also due to metal-to-ligand charge transfer.

Electrospray Mass Spectra

This technique can be developed to examine the selectivity of ligands by "challenging" a mixture of ligands with a relatively small concentration of a particular metal ion and using ES-MS to determine the abundance of species in the solution. It has long been postulated that the ion abundances, as revealed by mass spectrometry, should correlate with the concentration of species in solution. It would also be possible to investigate the selectivity of a ligand for a particular metal ion, as we have done in our preliminary work, by "challenging" the ligand with a solution of several metal ions of equimolar concentration and determining the abundance of each complex by ES-MS. Similar work has been recently reported for complexes of crown ethers with alkali metal cations [12].

The potential of ES-MS for characterisation of coordination complexes has been realised by several research groups over recent years [13–17]. However, use of this technique to examine labile complex systems in the presence of potentially competing metal ions has not been widely investigated. We have studied the copper(I) and copper(II) complexes in the presence of added silver(I) and found clear evidence for metal ion exchange. The relative abundance has been assumed to reflect the relative concentrations of species present in solution. Thus relative stabilities can be deduced from the electrospray mass spectra when a complex is challenged with another metal ion or a ligand solution is reacted with a mixed solution of metal ions. All assignments are based on ^{109}Ag, ^{63}Cu, and the most common isotopes of the other elements.

All the electrospray mass spectral data of the complexes are listed in Table VI. The electrospray mass spectrum of compound $[CuL^1](ClO_4)_2$ was obtained in acetonitrile solution. The cluster of peaks at $m/z = 370.0$ corresponds to the species $[CuL^1]^+$. Small peaks for $[CuL^1ClO_4]^+$ at $m/z = 469$ were found and ions corresponding to $[CuL^1]^{2+}$ at $m/z = 185.0$ were present as well. For the ES-MS spectrum of the $[AgL^1]ClO_4$ in acetonitrile, the peaks at $m/z = 416.0$ are attributed to the species $[AgL^1]^+$. Electrospray mass spectra for the copper(I) complex $[CuL^1]ClO_4$ (in acetonitrile) were also collected. The peaks at $m/z = 370.0$ correspond to $[CuL^1]^+$. The ES-MS spectrum of the reduced protonated ligand L^2 shows a peak at $m/z = 312$ corresponding to the protonated $[L^2H]^+$. The ES-MS spectra of the copper(II) complex $[CuL^2](ClO_4)_2$ show peaks at $m/z = 373.0$ corresponding to the species $[CuL^2 - H]^+$, and small peaks for $[CuL^2ClO_4]^+$ at $m/z = 473.0$ were found. The consistent observation of a peak at $m/z = 373$ for the copper(II) complex of L^2 indicates that the singly charged cation is most easily formed through the loss of a single proton, presumably from a hydrogen atom bound to a nitrogen atom in the reduced ligand.

When the ligand L^2 alone is treated with $Cu(ClO_4)_2$, major peaks in the mass spectrum are found at $m/z = 373.0$ $[CuL^2{-}H]^+$, $m/z = 187.0$ $[CuL^2]^{2+}$, $m/z = 473.0$ $[CuL^2ClO_4]^+$ and a relatively small peak at $m/z = 312$ $[L^2H]^+$. When the free ligand L^2 was reacted with excess (100-fold) $AgNO_3$, the peak at $m/z = 420.0$ indicate the formation of $[AgL^2]^+$; however, the intensity of the peak at $m/z = 312$ from protonated

TABLE VI ES-MS data for complexes of L^1 and L^2 with Ag^+ , Cu^{2+} and Cu^+

Complex mixture	*Ions* (*m/z*)
$[CuL^1](ClO_4)_2$	$[CuL^1]^+$ (370.0); $[CuL^1ClO_4]^+$ (469.0); $[CuL^1]^{2+}$ (185.0)
$[CuL^1](ClO_4)$	$[CuL^1]^+$ (370.0)
$[AgL^1](ClO_4)$	$[AgL^1]^+$ (416.0)
$[CuL^2](ClO_4)_2$	$[CuL^2 - H]^+$ (373.0); $[CuL^2ClO_4]^+$ (473.0); $[CuL^2]^{2+}$ (187.0)
$[CuL^2](ClO_4)_2 + [Ag^+]$	$[CuL^2{-}H]^+$ (373.0); $[AgL^2]^+$ (420.0); $[CuAgL^2]^{2+}$ (241.9); $[CuL^2]^{2+}$ (187.0)
$L^2 + [Ag^+]$	$[AgL^2]^+$(420.0); $[HL^2]^+$ (312.0); $[AgHL^2ClO_4]^+$(520.0)
$L^2 + [CuL^2](ClO_4)_2 + [Ag^+]$	$[CuL^2 - H]^+$ (373.0); $[AgL^2]^+$ (420.0); $[HL^2]^+$ (312.0); $[CuL^2ClO_4]^+$ (473.0)

L^2 is much greater than that for $[AgL^2]^+$. This suggests that the formation constant for the silver(I) complex of L^2 is relatively low.

In order to estimate the relative stability of the complexes, formed in the ES source, we measured the mass spectra for mixtures of solutions of $[CuL^2]^{2+}$ and $AgNO_3$ over a period of time, with the peak intensity assumed to reflect the population of various species in solution. When $[CuL^2]^{2+}$ was treated with increasing amounts of added silver(I) ion (the ratio of $Ag^+/[CuL^2]^{2+}$ used were 1:1, 5:1, 10:1, 20:1, 50:1 and 100 : 1), three major observations were made: (i) peaks corresponding to $[CuL^2-H]^+$ at $m/z = 373.0$, $[AgL^2]^+$ at $m/z = 420.0$ and $[CuAgL^2]^{2+}$ at $m/z = 241.9$ were detected (the calculated isotopic distribution pattern agrees with the observed pattern for $[CuAgL^2]^{2+}$); (ii) the intensity of $[AgL^2]^+$ peaks increased as the ratio $Ag^+/[CuL^2]^{2+}$ increased; (iii) when Ag^+ was added in 100-fold excess, the major peaks corresponded to $[AgL^2]^+$ at $m/z = 420$ and $[AgL^2ClO_4+H]^+$ at $m/z = 520$. The observation of a heterobinuclear ion is most important and suggests that the macrocycle is capable of simultaneously binding a copper(II) ion, possibly through the N_3 donor atoms, and a silver(I) ion, presumably through the sulfur donor atoms. This strongly implies that metal ion exchange in solution occurs in a stepwise process and depends on the thermodynamic stability of the complex ion.

The relatively high concentration of silver(I) needed to drive the reaction forward suggests that the thermodynamic stability of the copper(II) complex is greater than that of the silver(I) analogue. The results suggest that ES-MS may be applicable in the study of both kinetic and thermodynamic phenomena of labile complexes in solution.

References

[1] P. Jayaweera, A.T. Blades, M.G. Ikonomou and P. Kebarle, *J. Am. Chem. Soc.* **112**, 2452 (1990).

[2] V. Katta, S.K. Chowdhury and B.T. Chait, *J. Am. Chem. Soc.* **112**, 5348 (1990).

[3] F. Bitsch, C.O. Dietrich-Buchecker, A.K. Khemiss, J.P. Sauvage and A.V. Dorsselaer, *J. Am. Chem. Soc.* **113**, 4023 (1991).

[4] P.M. Fitzsimmons and S.C. Jackels, *Inorg. Chim. Acta* **246**, 301 (1996).

[5] S.M. Nelson, *Pure Appl. Chem.* **52**, 2461 (1980); D.E. Fenton, *Pure Appl. Chem.* **58**, 1437 (1986).

[6] L.F. Lindoy and D.H. Busch, In: W.L. Jolly (Ed.), Preparative Inorganic Reactions (Wiley-Interscience, New York, 1972), Vol. 6, p.2.

[7] M.G.B. Drew, C. Cairns, S.G. McFall and S. M. Nelson, *J. Chem. Soc, Dalton Trans.* 2020 (1980).

[8] R.W. Hay, P.M. Gidney and G.A. Lawrance (1980). *J. Chem. Soc*, *Dalton Trans.* 779.

[9] A.D. Rae, RAELS– A Comprehensive Least-Squares Refinement Program (Australian National University, Canberra, 1997).

[10] C.K. Johnson, 'ORTEP-II' (Oak Ridge National Laboratory, Oak Ridge, TN, 1976).

[11] A.T. Baker, D.C. Craig and P. Singh, *Aust. J. Chem.*, **44**, 1659 (1991).

[12] M. Bartoszek, H. Graubaum, D. Wendland and R. Dambowski, *Eur. Mass Spectrom.* **5**, 81 (1999).

[13] R. Colton, J.C. Traeger and V. Tedesco, *Inorg. Chem.* **31**, 3865 (1992).

[14] P.S. Bates D. Parker and B.N. Green, *J. Chem. Soc.*, *Chem. Commun.* **693** (1993).

[15] R. Colton, B.D.James, I.D. Potter and J.C. Traeger (1993). *Inorg. Chim. Acta*, **32**, 2626.

[16] S.R. Wilson, A. Yasmin and Y. Wu, *J. Organomet. Chem.* **486**, 243 (1995).

[17] Sutrisno, Y. Baran, G.A. Lawrance, E.I. von Nagy-Felsobuki, D.T.Richens and H. Xiao, *Inorg. Chem. Commun.* **2**, 107 (1999).