Closely Related Macrocyclic and Acyclic Tridentate, Pyridine Derivatives, containing Sulphur, and their Complexes. Crystal Structures of {Dichloro-3,10-dithia-16-azabicyclo[10.3.1]hexadeca-1(16),12,14-triene}copper(II) and [2,6-bis(ethylthiomethyl)pyridine]dichlorocopper(II) †

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Four closely related, tridentate, pyridine derivatives, containing sulphur, three of them macrocyclic, 3,10-dithia-16-azabicyclo[10.3.1]hexadeca-1(16),12,14-triene (L^1), 3,8-dithia-14-azabicyclo-[8.3.1]tetradeca-1(14),10,12-triene (L^2), 3,7-dithia-13-azabicyclo[7.3.1]trideca-1(13),9,11-triene (L^3), and one acyclic, 2,6-bis(ethylthiomethyl)pyridine (L^4), have been prepared. All contain the same co-ordination elements (NS_2) structurally placed in the same fashion, sulphur–methylene–pyridine–methylene–sulphur. Copper complexes of all the ligands and the palladium complex of L^1 have also been prepared. The molecular structures of the complexes [CuL^1Cl_2] and [CuL^4Cl_2] are described. The latter is monoclinic, space group $I2/c$, with a = 14.669(6), b = 7.418(4), c = 29.412(8) Å, β = 103.03(4)°, and Z = 8. The former is monoclinic, space group $P2/a$ with a = 14.677(9), b = 7.555(1), c = 29.969(4) Å, β = 101.00(2)°, and Z = 8. The different reactivity of the macrocycle ligand L^1 with respect to that of L^4 is discussed.

The chemistry of transition-metal tridentate ligands containing N and/or O or quadridentates containing N and S as donor atoms is well known and documented. On the contrary, not much information, especially structural, is available on tridentate NS_2 ligands (S = thioether).

We are very interested in comparing macrocyclic and acyclic ligands with structurally similar active sites in order to understand the true nature of the macrocyclic effect in these compounds. In this paper we report on the synthesis of four tridentate pyridine derivatives, containing sulphur, three of them macrocyclic, 3,10-dithia-16-azabicyclo[10.3.1]hexadeca-1(16),12,14-triene (L^1), 3,8-dithia-14-azabicyclo[8.3.1]tetradeca-1(14),10,12-triene (L^2), 3,7-dithia-13-azabicyclo[7.3.1]trideca-1(13),9,11-triene (L^3), and one acyclic, 2,6-bis(ethylthiomethyl)pyridine (L^4). All contain the same co-ordination elements (NS_2) structurally placed in the same fashion, sulphur–methylene–pyridine–methylene–sulphur.

Several copper and palladium complexes are also reported. In addition, we report on the molecular structures of the copper(II) chloride complexes of two of the ligands, L^1 and L^4, in order to discuss their different reactivities.

Experimental

Unless specifically mentioned, all ligands were synthesized under a nitrogen atmosphere. Dehydrated and deoxygenated solvents were used. Methanol was dehydrated with Mg. Solvents were placed under vacuum to eliminate the dissolved oxygen. In all cases this treatment was sufficient for the reaction.

Microanalysis (C, H, and N) were performed in our analytical laboratory on a Perkin-Elmer 240-B instrument. Proton n.m.r. spectra were recorded on a Bruker WF 80SY spectrometer in $CDCl_3$ solution, electronic spectra on a Kontron UVIKON-860 spectrophotometer in CH_2Cl_2 solution, and i.r. spectra on a Perkin-Elmer 240 FT spectrophotometer as KBr pellets. All compounds reported in this paper analyzed correctly (Table 1)

Table 1. Analytical and physical data

			Analysis */%		
Compound	Colour	Yield/%	C	H	N
L^1	White	12.7	40.3	4.9	3.6
			(40.5)	(4.9)	(3.5)
L^2	White	10.7	36.7	4.2	3.9
			(37.2)	(4.6)	(3.25)
L^3	White	9.3	34.7	3.8	4.1
			(35.4)	(4.15)	(3.95)
L^4	White	49.0	58.0	7.3	6.1
			(58.15)	(7.5)	(6.15)
[CuL^1Cl_2]	Green	47.0	40.3	4.9	3.6
			(40.5)	(4.9)	(3.5)
[PdL^1Cl_2]	Orange	45.4	29.9	3.7	2.7
			(29.05)	(3.75)	(2.7)
[CuL^2Cl_2]	Green	55.7	36.7	4.2	3.9
			(37.2)	(4.6)	(3.25)
[CuL^2Br_2]	Maroon	47.3	29.4	3.4	3.1
			(31.0)	(3.55)	(3.2)
[CuL^3Cl_2]	Green	34.5	34.7	3.8	4.1
			(35.4)	(4.15)	(3.95)
[CuL^4Cl_2]	Green	65.0	36.5	4.1	4.8
			(36.5)	(3.85)	(4.75)
[CuL^4Br_2]	Maroon	40.0	29.9	3.1	3.7
			(29.3)	(3.1)	(3.75)
[$CuL^4(NO_3)$][NO_3]	Green	41.1	32.1	10.3	4.2
			(31.85)	(10.15)	(4.15)

* Calculated values are given in parentheses.

Synthesis of 2,6-*Bis*(*ethylthiomethyl*)*pyridine* (L^4).—This compound has been already reported by us.[1]

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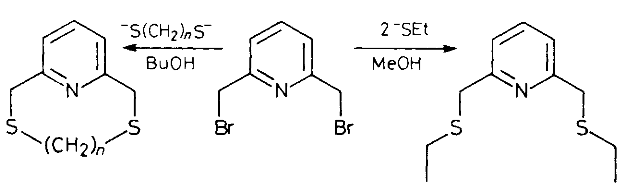
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Scheme.

Metal Complexes of 2,6-*Bis*(*ethylthiomethyl*)*pyridine*.—The complexes of Ni^{II},[1] Co^{II},[2] Zn^{II},[1] and Cd^{II}[2] have already been described by us.

Copper. Equimolar solutions of the appropriate ligand and metallic salts in methanol were mixed in all cases. In a typical experiment, L^4 (0.4 g, 1.7 mmol) dissolved in methanol (5 cm^3) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.3 g, 1.7 mmol) in methanol (5 cm^3). A green precipitate appeared which was filtered off, washed with methanol, and vacuum dried.

Synthesis of the Macrocyclic Ligands.—Two solutions, A and B, were mixed, under high dilution conditons and a nitrogen atmosphere, in 1.5 l of dry butanol.

3,10-*Dithia*-16-*azabicyclo*[10.3.1]*hexadeca*-1(16),12,14-*triene* (L^1). Solution A was formed by 2,6-bis(bromomethyl)-pyridine (4.9 g, 18.5 mmol) dissolved in butanol (50 cm^3). Solution B was hexane-1,6-dithiol (2.86 cm^3, 18.5 mmol) and KOH (2.1 g, 37 mmol), in butanol (50 cm^3).

3,8-*Dithia*-14-*azabicyclo*[8.3.1]*tetradeca*-1(14),10,12-*triene* (L^2). Solution A was 2,6-bis(bromomethyl)pyridine (5.8 g, 21.8 mmol) in butanol (50 cm^3). Solution B was butane-1,4-dithiol (2.56 cm^3, 21.8 mmol) and KOH (2.45 g, 43.6 mmol) in methanol (50 cm^3).

3,7-*Dithia*-13-*azabicyclo*[7.3.1]*trideca*-1(13),9,11-*triene* (L^3). Solution A was 2,6-bis(bromomethyl)pyridine (6.12 g, 23.1 mmol) in butanol (50 cm^3). Solution B was propane-1,3-dithiol (2.32 cm^3, 23.1 mmol) and KOH (2.59 g, 46.2 mmol) in butanol (50 cm^3).

In all cases the mixture was refluxed for 1 h after completion of the addition (17 h). A white precipitate of KCl was obtained which was rejected. The clear coloured solution was evaporated until an oil appeared. The oil was dissolved in benzene, washed with water and Na_2CO_3, and dried over $MgSO_4$. The benzene solution was evaporated and the oil obtained chromatographed over alumina using benzene as the eluant. The first fraction was evaporated and the resulting oil dissolved in light petroleum (40—70 °C). The solution was kept in a freezer. A white solid was obtained, which was filtered off, washed, and dried under vacuum.

Copper Complexes of the Macrocyclic Ligands.—Equimolar solutions of the appropriate ligand and metallic salts in methanol were mixed in all cases. In a typical experiment, L^1 (0.2 g, 0.79 mmol) dissolved in methanol (5 cm^3) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.135 g, 0.79 mmol) in methanol (5 cm^3). A green precipitate appeared which was filtered off, washed with methanol and vacuum dried.

Palladium Complex.—The ligand L^1 (0.1 g, 0.4 mmol) dissolved in methanol was added to a solution of $PdCl_2 \cdot 2H_2O$ (0.084 g, 0.4 mmol) and NEt_4Cl (0.087 g, 0.8 mmol) in methanol. A yellow precipitate appeared which was filtered off, washed, and dried.

X-*Ray Structure Determinations*.—The green single crystals of $[CuL^4Cl_2]$ are monoclinic, space group $I2/c$ with a = 14.669(6), b = 7.418(4), c = 29.412(8) Å, β = 103.03(4)°, U = 3.1182 $Å^3$, Z = 8, D_c = 1.54 Mg m^{-3}, μ = 19.9 cm^{-1}. The green single crystals of $[CuL^1Cl_2]$ are monoclinic, space group $P2/a$ with a = 14.677(9), b = 7.555(1), c = 29.969(4) Å, β = 101.00(2)°, U = 3.2620 $Å^3$, Z = 8, D_c = 1.58 Mg m^{-3}, μ = 19.9 cm^{-1}.

X-Ray diffraction data for $[CuL^4Cl_2]$ and $[CuL^1Cl_2]$ at 294 K were collected with an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) on a 0.3 × 0.35 × 0.5 ($[CuL^4Cl_2]$) or 0.7 × 0.28 × 0.37 mm ($[CuL^1Cl_2]$) prismatic crystal. Reflections were measured at the azimuth position corresponding to a minimum absorption using an imaginary crystal with finite but small thickness having an infinitely large surface area (flat psi mode).

Using the ω—2θ scan technique, 5 904 reflections with $2\theta < 50°$ ($-16 < h < 16, 0 < k < 8, 0 < l < 34$) for $[CuL^4Cl_2]$ or 5 449 reflections with $2\theta < 47°$ ($-16 < h < 16$, $0 < k < 8$, $0 < l < 33$) for $[CuL^1Cl_2]$ were obtained. These non-unique data were averaged and the resulting 2 827 ($[CuL^4Cl_2]$) or 5 374 ($[CuL^1Cl_2]$) intensities were corrected for Lorentz and polarization effects; only 1 345 ($[CuL^4Cl_2]$) or 3 546 ($[CuL^1Cl_2]$) were considered observed with $F > 3\sigma(F)$ or $F > 2.5\sigma(F)$ respectively.

The atomic co-ordinates of the Cu and Cl atoms were located by direct methods.[3] Subsequent Fourier difference syntheses combined with refinement of located atoms resulted in a complete model of the structure. This model was refined with SHELX 76[4] using anisotropic thermal parameters giving an R factor of 0.09 and R' = 0.076 ($[CuL^4Cl_2]$) or R = 0.085, R' = 0.094 ($[CuL^1Cl_2]$) [$w = 1/\sigma^2(F) + 0.000\,04F^2$]. The hydrogen atoms were introduced in calculated positions and refined with a global thermal parameter. On a final Fourier difference synthesis the maximum height (0.6 e $Å^{-3}$) is located near to S(2) for $[CuL^4Cl_2]$ and near C(14) (0.86 Å) (2.0 e $Å^{-3}$) for $[CuL^1Cl_2]$; this fact together with the significantly high value of B_{eq} for the C atoms of the hexane chain suggest a possible slight positional disorder of this fragment in contrast with the well positioned atoms of the equivalent fragment of the other molecule in the asymmetric unit of $[CuL^1Cl_2]$. The largest shift/error in the final cycle is 0.31 ($[CuL^4Cl_2]$) and 0.26 ($[CuL^1Cl_2]$), respectively. The scattering factors were taken from ref. 5.

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

Results and Discussion

The close relation between the acyclic and macrocyclic ligands is evidenced by the general synthetic procedure used to obtain them (Scheme).

In all cases the compounds were prepared by nucleophilic substitution of an halogen atom bonded to a saturated carbon atom by a thiolate ion in a protonic polar solvent (methanol, S_N1 reaction mechanism). The geometrical arrangement of the co-ordination sites in all these ligands makes them suitable for comparison purposes.

Proton N.M.R. Spectra of the Ligands.—The spectra were registered in $CDCl_3$ solution and display, in all cases, four signals. The first one (L^1, 7.9, m, 3; L^2, 7.4, m, 3; L^3, 7.4, m, 3) is a multiplet integrating for three protons and is assigned to the protons of the pyridine ring. The second (L^1, 3.9, s, 4; L^2, 3.85, s, 4; L^3, 3.95, s, 4) is a singlet integrating for four protons and is assigned to the protons bonded to the two carbon atoms between the pyridine ring and the sulphur atoms. The third (L^1, 2.55, m, 4; L^2, 2.95, m, 4; L^3, 2.92, t, 4) integrates for four protons and is assigned to the methylene protons next to the sulphur atoms at the aliphatic chain. This signal appears as a multiplet except in the case of the ligand L^3. In this case the signal is a well defined triplet due to the splitting of the two protons of the central methylene. The fourth signal (L^1, 1.55, m, 8; L^2, 1.3, m, 4; L^3, 1.28, qnt, 2) integrates for eight, four, or two protons according to the aliphatic chain length of each ligand and is assigned to the rest of the aliphatic chain protons. This signal is well resolved in the case of the ligand L^3; it appears as a quintuplet due to the splitting of the four protons next to the sulphur atoms. The ^{1}H-n.m.r. spectra are in agreement with the formula proposed.

The ^{1}H-n.m.r. spectra of the Ligand L^4 and the changes observed in the diamagnetic complex $[ZnL^4Br_3]$ have already been discussed.[1]

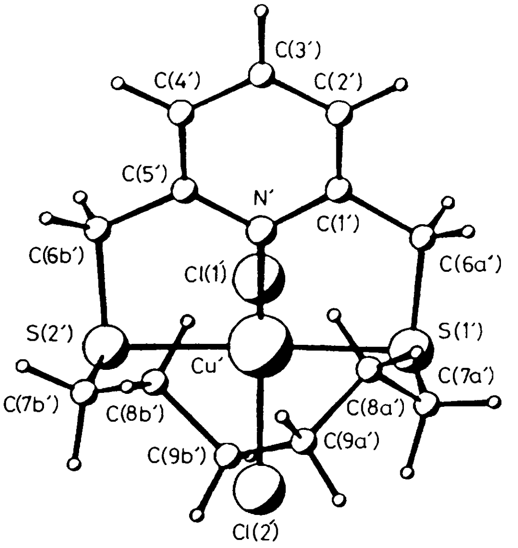
Electronic Spectra.—All the macrocyclic ligands present two bands in the u.v. region at 210—215 ($\varepsilon \approx 6\,860$) and 270—275 nm ($\approx 4\,700$ dm^3 mol^{-1} cm^{-1}). The complexes synthesized are only slightly soluble in methanol, but they undergo decomposition in this solvent as is evidenced by the change in colour of the solutions. The acyclic ligand, L^4, also presents two bands in the u.v. region at 220 ($\varepsilon \approx 4\,000$) and 266 nm ($\varepsilon \approx 4\,000$ dm^3 mol^{-1} cm^{-1}). The copper complexes of this ligand are slightly soluble in CH_2Cl_2 and their electronic spectra were recorded in this solvent. A broad band at 745—796 nm appears for all of them, which is typical for five-co-ordinated copper(II) complexes.[6]

I.r. Spectra.—The i.r. spectra of the ligands and complexes are intricate. Bands due to the organic ligands are of little value for characterization purposes. Only several bands assigned to the pyridine ring show slight shifts due to the metal-ion co-ordination, but they are difficult to systematize as is usual for pyridine derivative ligands.[7]

Copper nitrate complex. The i.r. spectra of nitrate-containing complexes are a valuable tool for elucidation of their stereochemistry. Frequently, such studies are based on the behaviour of the ν_3 (E', D_{3h}) band, which is very sensitive to the co-ordination mode of the nitrate group. In general there are several bands due to the organic ligands in the N–O stretching mode region, which make difficult the analysis of the ν_3 band. Lever and Mantovani[8] have demonstrated the utility of the $\nu_1 + \nu_4$ (E', D_{3h}) combination band for structural purposes. This band appears near 1 750 cm^{-1} and is not generally overlapped by other ligand bands.

The copper complex $CuL^4(NO_3)_2$ exhibits three bands in this region of 1 716, 1 748, and 1 763 cm^{-1}. This behaviour is compatible with the presence of an ionic nitrate group (1 748 cm^{-1}) and a bidentate co-ordinated nitrate (1 716 and 1 763 cm^{-1}) in the molecule. The presence of two different nitrate groups is corroborated in the N–O stretching region. In this zone there are one strong band at 1 385 cm^{-1} attributable to the ν_3 (E', D_{3h}) mode of the ionic NO_3^- group and two strong bands at 1 484 and 1 285 cm^{-1} assigned to the splitting of the ν_3 mode by bidentate co-ordination.[7] This compound could be formulated as $[CuL^4(NO_3)][NO_3]$ the Cu^{II} being five-co-ordinated.

Molecular Structures of $[CuL^4Cl_2]$ *and* $[CuL^1Cl_2]$.—Tables 2 and 3 report selected bond lengths and angles for the two compounds, Tables 4 and 5 the corresponding atomic coordinates. Figure 1 shows a perspective view of the $[CuL^4Cl_2]$ molecule with atom numbering. The co-ordination polyhedron



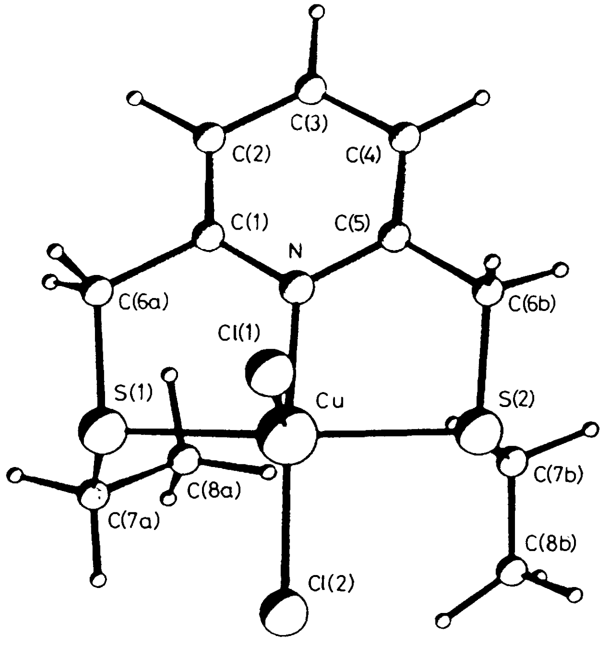


Figure 1. Molecular structure with atom numbering of $[CuL^4Cl_2]$

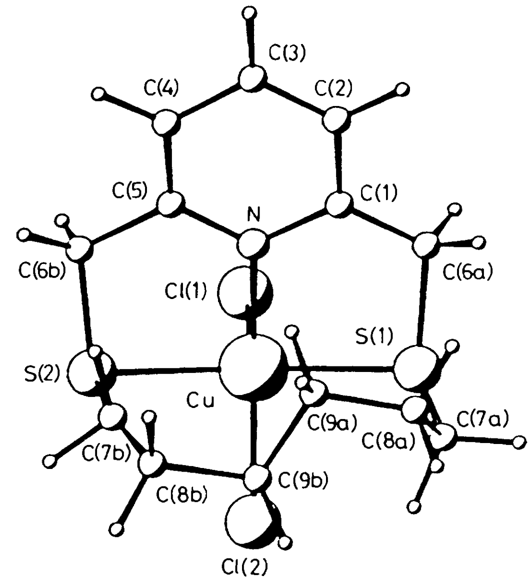


Figure 2. Molecular structure with atom numbering of $[CuL^1Cl_2]$

Table 2. Selected bond lengths (Å) and angles (°) with their estimated standard deviations (e.s.d.s) for $[\mathrm{CuL^{4}Cl_{2}}]$

Cl(1)–Cu	2.428(3)	C(6a)–S(1)	1.802(13)
Cl(2)–Cu	2.242(4)	C(7a)–S(1)	1.786(14)
S(1)–Cu	2.344(4)	C(6b)–S(2)	1.781(13)
S(2)–Cu	2.358(4)	C(7b)–S(2)	1.828(17)
N–Cu	2.016(10)		
Cl(2)–Cu–Cl(1)	106.3(1)	N–Cu–S(1)	85.8(3)
S(1)–Cu–Cl(1)	99.4(1)	N–Cu–S(2)	84.7(3)
S(1)–Cu–Cl(2)	91.4(1)	C(6a)–S(1)–Cu	97.2(5)
S(2)–Cu–Cl(1)	97.2(1)	C(7a)–S(1)–Cu	107.2(6)
S(2)–Cu–Cl(2)	92.1(1)	C(7a)–S(1)–C(6a)	103.8(7)
S(2)–Cu–S(1)	161.3(1)	C(6b)–S(2)–Cu	94.9(5)
N–Cu–Cl(1)	93.5(3)	C(7b)–S(2)–Cu	105.5(6)
N–Cu–Cl(2)	160.2(3)	C(7b)–S(2)–C(6b)	99.2(8)

about the Cu atom can be described as a square pyramid. The mean plane defined by the base atoms S(1), S(2), N, Cl(2) has a root-mean-square deviation (r.m.s.d.) of 0.004 Å and the Cu atom is 0.367 Å out of this plane inside the polyhedron. The Cl(1) atom occupies the apical position and the angle between the mean planes defined by the base atoms and S(1), S(2), Cl(1) is 93.4° and with N, Cl(1), Cl(2) is 90.8°. However, the conformation of the polyhedron is distorted by the different atom types and, in particular, by the Cl(1) ··· Cl(2) repulsion [Cl(1)–Cu–Cl(2) 106.3(1)°]. The ethyl groups are oriented in the opposite direction to the Cl(1) atom, yielding a hole in the sixth co-ordination position of Cu. The carbon atoms C(6a) and C(6b) are not coplanar with the pyridine ring, as would be expected from the sp^2 character of the pyridine carbons, probably due to the metal co-ordination. It is interesting to note the different Cu–Cl distances in the molecule; the $\mathrm{Cu{-}Cl_{basal}}$ distance is 2.242 Å, while $\mathrm{Cu{-}Cl_{apical}}$ is 2.428 Å, as is usual in d^9 ions having C_{4v} five-co-ordination. On the other hand the Cu–S distances are similar (2.34, 2.36 Å) and comparable with those in the literature.[9]

Figure 2 shows a perspective view of the two $[\mathrm{CuL^{1}Cl_{2}}]$ molecules in the asymmetric unit. The co-ordination polyhedron about the Cu atoms can be described as a distorted square pyramid. The mean planes defined by the base atoms S(1), S(2), N, Cl(2) and S(1′), S(2′), N′, Cl(2′) have r.m.s.d. of 0.126 and 0.088 Å respectively. The Cu atoms are 0.381 and 0.375 Å out of these planes inside the polyhderon. The Cl(1) [Cl(1′)] atom occupies the apical position. The angles between the mean planes defined by the base atoms and S(1), S(2), Cl(1) [S(1′), S(2′), Cl(1′)] are 88.6 and 90.4°, respectively, and with N, Cl(1), Cl(2) [N′, Cl(1′), Cl(2′)] are 91.1 and 91.2°, respectively. However, the conformations of these polyhedra are distorted by the different atom types (see Table 3). The pyridine rings are nearly planar (r.m.s.d. 0.017 and 0.014°, respectively) and form dihedral angles of 11.3 and 10.4° with the corresponding mean planes of the base atoms of the copper polyhedra.

The C(6a) and C(6b) atoms slightly deviate towards Cl(1) with respect to the mean plane of base atoms (0.04 and 0.34°, respectively), similarly for C(6a′) and C(6b′) with respect to the pyridine ring (0.00 and 0.12°) and to the base atoms (0.15 and 0.24°). The hexane chains are oriented in opposite directions to Cl(1). Summarizing, the two independent molecules are similar except for conformations of the hexane chains.

Table 3. Selected bond lengths (Å) and angles (°) with their e.s.d.s for $[\mathrm{CuL^{1}Cl_{2}}]$

Cl(2)–Cu	2.247(3)	Cl(2′)–Cu′	2.260(4)
Cl(1)–Cu	2.422(4)	Cl(1′)–Cu′	2.410(4)
S(1)–Cu	2.343(4)	S(2′)–Cu′	2.358(3)
S(2)–Cu	2.350(4)	S(1′)–Cu′	2.338(3)
N(1)–Cu	2.000(7)	N(1′)–Cu′	2.001(10)
C(6a)–S(1)	1.840(11)	C(6b′)–S(2′)	1.804(15)
C(7a)–S(1)	1.803(12)	C(7b′)–S(2′)	1.780(17)
C(6b)–S(2)	1.770(12)	C(6a′)–S(1′)	1.798(16)
C(7b)–S(2)	1.817(15)	C(7a′)–S(1′)	1.836(16)
Cl(1)–Cu–Cl(2)	102.1(1)	Cl(1′)–Cu′–Cl(2′)	101.3(1)
S(1)–Cu–Cl(2)	92.4(1)	S(2′)–Cu′–Cl(2′)	91.8(1)
S(1)–Cu–Cl(1)	101.5(1)	S(2′)–Cu′–Cl(1′)	99.6(1)
S(2)–Cu–Cl(2)	91.6(1)	S(1′)–Cu′–Cl(2′)	91.8(1)
S(2)–Cu–Cl(1)	102.7(2)	S(1′)–Cu′–Cl(1′)	102.7(1)
S(2)–Cu–S(1)	154.0(1)	S(1′)–Cu′–S(2′)	156.2(1)
N(1)–Cu–Cl(2)	166.1(3)	N(1′)–Cu′–Cl(2′)	164.5(3)
N(1)–Cu–Cl(1)	91.8(3)	N(1′)–Cu′–Cl(1′)	94.2(3)
N(1)–Cu–S(1)	86.0(2)	N(1′)–Cu′–S(2′)	84.9(3)
N(1)–Cu–S(2)	83.9(2)	N(1′)–Cu′–S(1′)	85.3(3)
C(6a)–S(1)–Cu	96.4(4)	C(6b′)–S(2′)–Cu′	95.6(4)
C(7a)–S(1)–Cu	110.6(4)	C(7b′)–S(2′)–Cu′	110.9(5)
C(7a)–S(1)–C(6a)	106.3(6)	C(7b′)–S(2′)–C(6b′)	101.7(7)
C(6b)–S(2)–Cu	95.6(4)	C(6a′)–S(1′)–Cu′	96.8(4)
C(7b)–S(2)–Cu	100.0(5)	C(7a′)–S(1′)–Cu′	108.8(5)
C(7b)–S(2)–C(6b)	103.1(6)	C(7a′)–S(1′)–C(6a′)	103.0(7)
C(8a)–C(7a)–S(1)	123.7(10)	C(8b′)–C(7b′)–S(2′)	117.9(12)
C(9a)–C(8a)–C(7a)	121.5(14)	C(9b′)–C(8b′)–C(7b′)	111.2(13)
C(7b)–C(9a)–C(8a)	106.9(11)	C(9a′)–C(9b′)–C(8b′)	112.6(14)
C(8b)–C(9b)–C(9a)	102.7(11)	C(8a′)–C(9a′)–C(9b′)	112.2(14)
C(7b)–C(8b)–C(9b)	103.2(11)	C(7a′)–C(8a′)–C(9a′)	115.6(14)
C(8b)–C(7b)–S(2)	157.0(10)	C(8a′)–C(7a′)–S(1′)	117.3(11)

Table 4. Fractional atomic co-ordinates for non-hydrogen atoms ($\times 10^4$) with their e.s.d.s for $[\mathrm{CuL^{4}Cl_{2}}]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	7 132(1)	1 756(3)	6 196(1)
Cl(1)	7 338(2)	3 333(6)	5 503(1)
Cl(2)	8 144(3)	3 005(6)	6 801(1)
S(1)	5 891(2)	3 441(6)	6 359(1)
S(2)	8 157(2)	−661(6)	6 158(1)
N	6 136(6)	109(17)	5 834(3)
C(1)	5 211(8)	471(23)	5 774(4)
C(2)	4 517(9)	−571(26)	5 541(5)
C(3)	4 779(9)	−2 188(26)	5 370(4)
C(4)	5 717(9)	−2 630(24)	5 413(4)
C(5)	6 369(9)	−1 457(21)	5 647(4)
C(6a)	4 961(9)	2 317(22)	5 953(4)
C(7a)	5 737(12)	2 730(26)	6 917(5)
C(8a)	5 768(11)	665(28)	6 975(5)
C(6b)	7 400(8)	−1 721(22)	5 673(4)
C(7b)	8 017(14)	−2 223(24)	6 618(6)
C(8b)	8 553(22)	−1 744(35)	7 060(7)

Conclusion

Studies with the ligand $\mathrm{L^4}$ had been reported by us[1,2] and with similar ligands by, Parker *et al.*[10] Of interest in the present work is the dissimilarity in reactivity exhibited by the ligands towards first-row transition-metal ions. Ligand $\mathrm{L^4}$ reacts with $\mathrm{Cu^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Cd^{II}}$, $\mathrm{Ni^{II}}$, and $\mathrm{Co^{II}}$ and every anion tested so far ($\mathrm{X = Cl^-, Br^-, NO_3^-}$, or $\mathrm{SCN^-}$). This ligand forms mononuclear compounds with $\mathrm{Ni^{II}}$, $\mathrm{Zn^{II}}$ (trigonal-bipyramidal co-ordination for the metal ion),[1] and $\mathrm{Cu^{II}}$ (square pyramid, as shown in this paper), and binuclear compounds with halide bridges for $\mathrm{Co^{II}}$ and $\mathrm{Cd^{II}}$[2] (octahedral co-ordination around the metal ion). On the contrary, $\mathrm{L^1}$ is more selective since it gives complexes only with $\mathrm{CuX_2}$ (X = Cl). It also reacts with palladium(II) salts, as expected from the soft character of the sulphur thioether atoms, but no further attempts were made, to obtain complexes with second- or third-row transition-metal ions with this macrocycle or the others.

Table 5. Fractional atomic co-ordinates for non-hydrogen atoms (× 10^4) with their e.s.d.s for [CuL^2Cl_2]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	7 119(1)	1 401(2)	1 191(1)	Cu′	6 158(1)	3 165(2)	3 848(1)
Cl(1)	7 310(2)	3 288(4)	562(1)	Cl(1′)	6 851(2)	1 506(4)	4 514(1)
Cl(2)	8 201(2)	2 470(4)	1 760(1)	Cl(2′)	6 764(2)	1 780(5)	3 303(1)
S(1)	5 915(2)	2 842(4)	1 459(1)	S(1′)	4 727(2)	1 752(4)	3 619(1)
S(2)	8 050(2)	−1 055(6)	1 101(2)	S(2′)	7 243(2)	5 492(4)	3 893(1)
N(1)	6 117(5)	9(10)	797(3)	N(1′)	5 467(6)	4 804(11)	4 190(3)
C(1)	5 185(7)	464(13)	797(4)	C(1′)	4 572(8)	4 450(15)	4 249(4)
C(2)	4 486(7)	−653(15)	530(4)	C(2′)	4 089(8)	5 583(15)	4 461(5)
C(3)	4 708(9)	−2 054(15)	294(5)	C(3′)	4 490(9)	7 140(18)	4 628(5)
C(4)	5 651(8)	−2 475(14)	332(4)	C(4′)	5 383(9)	7 519(15)	4 594(5)
C(5)	6 314(7)	−1 413(13)	569(4)	C(5′)	5 855(7)	6 320(13)	4 378(4)
C(6a)	4 965(8)	2 022(15)	1 015(4)	C(6a′)	4 160(9)	2 713(16)	4 042(5)
C(6b)	7 342(8)	−1 814(15)	591(4)	C(6b′)	6 870(9)	6 629(16)	4 356(5)
C(7a)	5 741(10)	1 864(14)	1 985(4)	C(7a′)	4 118(11)	2 778(19)	3 090(6)
C(7b)	7 743(12)	−2 526(16)	1 529(5)	C(7b′)	6 912(11)	7 016(19)	3 438(6)
C(8a)	5 438(10)	−16(14)	2 027(6)	C(8a′)	4 027(10)	4 845(19)	3 082(6)
C(8b)	7 350(13)	−3 046(15)	1 939(6)	C(8b′)	5 870(11)	7 241(17)	3 243(6)
C(9a)	5 917(8)	−1 485(17)	1 859(6)	C(9a′)	4 524(12)	5 833(23)	2 731(7)
C(9b)	6 939(8)	−1 316(15)	2 076(6)	C(9b′)	5 525(11)	5 834(19)	2 872(6)

Both compounds L^4 and L^1 have identical co-ordination sites (NS_2) in an identical conformation, the difference between them lying in the hydrocarbon chain, which is closed in L^1. *X*-Ray diffraction studies reported in this paper have shown the similarity between [CuL^4Cl_2] and [CuL^1Cl_2]. In each case the co-ordination polyhedron around the Cu^{II} is a distorted square pyramid, with no significant differences between them. So, one would expect similar structures for the compounds of a given metal ion with the two ligands.

The difference in reactivity cannot be strictly attributed to the macrocyclic nature of L^1, since upon co-ordination the hydrocarbon chains do not fully encircle the metal ion, but tend to lie 'perpendicular' to the plane defined by the S–pyridine–S moiety. The metal ion is co-ordinated in a exo-cycle fashion. We believe that these differences are also due to the disposition of the sulphur lone pairs. In L^4 these have a greater ability to accommodate a specific metal geometrical requirement than in L^1, whose disposition is dictated by the hydrocarbon chain conformation. Free orientation of the ethyl groups in L^4 could provide more flexibility to the sulphur lone pairs to co-ordinate different metal ions than in L^1, in which the lone pairs are more constricted due to the conformation of the hexane chain.

It is relevant that the co-ordinating properties of L^1 type ligands can be modulated by hydrocarbon chain variation and, on the other hand, the compounds described represent a nice example of how the molecular structure and hence the electronic structure and properties can be slightly varied by changing the inactive part of the molecule without changing the essential co-ordination site.

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