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SILVER(I), MERCURY(II) AND COPPER(I) COMPLEXES OF ACYCLIC AND MACROCYCLIC DITHIOETHER, *META*-XYLYL BASED LIGANDS

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Abstract—The compounds $[{HgL^1(NO_3)_x}]$ (L¹ = 6-oxa-3,9-dithiabicyclo[9,3,1] pentadeca-1(15),11,13-triene) (1), $[{AgL^2(NO_3)}_x]$ (L² = (1,3-bis(phenylthio)methyl) benzene) (2), $[{HgL^3Cl_2}_2]$ and $[{CuL^3Cl}_x]$ (L³ = (1,3-Bis(ethylthio)methyl)benzene) (3) and (4) have been synthesized and their structures determined by X-ray crystallography. Compounds (1) and (2) have linear polymeric chains of alternating trigonal silver(I) cations and bridging ligands bonded through the sulfur atoms. In both structures the nitrate anion retains coordination to the silver atom. Compound (3) is a dimeric complex. Each mercury(II) cation is bound to two bridging chlorine atoms, one terminal chlorine atom and one sulfur atom from the ligand. Compound (4) is a threedimensional polymer. Each Cu¹ cation has a distorted tetrahedral environment defined by two sulfur atoms of different L³ ligands and two bridging chlorine atoms. In each case the dithioether ligand acts as a bridging or monodentate ligand and does not chelate the metal.

Notable attention has been devoted in recent years to the development of new acyclic and macrocyclic polythioether ligands and the study of their complexing capabilities. In spite of the fact that the thioethers were formerly considered poor donors to the transition metal ions,¹ a great quantity of chemical and structural information regarding their complexes may now be found in the literature.² Two aspects have promoted much of the work on thioether coordination chemistry; firstly, the role of thioether binding in biological systems such as d-biotin³ and blue copper proteins⁴ and secondly, the parallel between the binding of soft, transition metal ions by soft, polythioether ligands and the binding of hard, Group 1 and 2 metal ions by hard polyoxyether ligands.² The latter aspect has become an important guide for researchers working in chemical recognition and transport phenomena of transition metal ions.⁵

Recently, we have developed membrane-based ion-selective electrodes (ISE) incorporating polythioethers as neutral carriers.^{6 8} Unexpectedly, a wide variety of these systems exhibit similar behaviour towards silver(I) cations.^{9,10} To gain further insight into the mechanisms of cation recognition by these membranes, we began with structural studies of the complexes of these ligands with some d^{10} cations. The study involved complexes of silver(I), mercury(II) and copper(I) ions, and the ISEs showed highest selectivity towards silver(I), whilst mercury(II) caused the greatest interference. Copper(I) forms a different type of coordination polymer which is included for comparison. Here we report

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the synthesis and structural determination of some silver (I), mercury(II) and copper(I) complexes with the dithioether containing ligands; 6-oxa-3,9-dithiabicyclo[9,3,1]pentadeca-1(15),11,13-triene (L^1), (1,3-bis(phenylthio)methyl)benzene (L^2) and (1,3-bis(ethylthiomethyl)benzene (L^3) (Scheme 1).



EXPERIMENTAL

Syntheses were carried out using standard Schlenk techniques under dry dinitrogen. Solvents were dried by conventional methods and distilled under dinitrogen. 6-Oxa-3,9-dithiabicyclo[9,3,1] pentadeca-1(15),11,13-triene (L¹) and 1,3-bis (ethylthiomethyl) benzene (L³) were prepared according to published procedures.^{7,9} Elemental analyses were performed in our microanalytical laboratory on a Carlo Erba EA-1108 instrument. ¹H and ¹³C{¹H} NMR were recorded on a Bruker 400 MHz AC instrument.

Preparations

1,3-Bis((phenylthio)methyl)benzene (L^2). Thiophenol (6.28 g, 57 mmol) was added to a stirred solution of KOH 85% (3.76 g, 57.0 mmol) in 1butanol (200 cm³). The mixture was refluxed for a further 30 min and added to a solution of 1,3dichlorobenzene (5 g, 28.5 mmol) in 1-butanol (100 cm³) and refluxed for 1 h more. The KCl precipitate was filtered off and the remaining solution was allowed to stand. On cooling, a white crystalline solid of L² precipitated, which was filtered off and vacuum dried. Yield: 41% (3.82 g). Found: C, 74.7; H, 5.7; S, 19.5. Calc. for C₂₀H₁₈S₂, C, 74.5; H, 5.6; S, 19.9%. ¹H NMR (400 MHz, CDCl₃), δ 4.05 (s, 4, S-CH₂-Ph), 7.14-7.29 (m, 14, Ph). ¹³C{¹H} NMR (100 MHz, CDCl₃), δ 38.97 S-CH₂-Ph), 126.43, 127.74, 128.67, 128.91, 129.39, 129.96, 136.34, 137.81 (Ph).

 $[{AgL^{1}(NO_{3})}_{\infty}]$ (1) AgNO₃ (0.07 g, 0.41 mmol) was slowly added to a stirred solution of L¹ (0.10

g, 0.41 mmol) in methanol (15 cm³). The resulting mixture was refluxed in the absence of light for 2 h, filtered and allowed to stand for 3 days at room temperature. A white crystalline solid of (1) precipitated which was filtered off and vacuum dried. Yield: 71% (0.120 g). Found: C, 34.7; H, 3.8; N, 3.2; S, 15.1. Calc. for $C_{12}H_{16}S_2O_4NAg$, C, 35.1; H, 3.9; N, 3.4; S, 15.6%.

[{AgL²(NO₃)}_∞] (2). In the absence of light, AgNO₃ (0.053 g, 0.31 mmol) was slowly added to a stirred solution of L² (0.1 g, 0.31 mmol) in methanol (100 cm³). The resulting mixture was refluxed for 36 h, filtered and allowed to stand for 48 h at room temperature. On standing colourless, prismatic crystals of (2) formed, which were filtered off and vacuum dried. Yield: 77% (0.119 g). Found: C, 49.1; H, 3.7; N, 2.5; S, 13.7. Calc. for C₂₀H₁₈S₂O₃NAg, 48.8; H, 3.7; N, 2.8; S, 13.0%. ¹H NMR (400 MHz, CDCl₃), δ 4.16 (s, 4, S—CH₂—Ph), 7.03–7.40 (m, 14, Ph). ¹³C{¹H} NMR (100 MHz, CDCl₃), δ 42.67 (S—CH₂—Ph), 128.45, 128.71, 128.77, 129.49, 132.24, 132.53, 136.40 (Ph).

[{HgL³Cl₂}₂] (**3**). HgCl₂ (0.12 g, 0.44 mmol) and concentrated HCl (0.5 cm³) were added to a solution of L³ (0.1 g, 0.44 mmol) in methanol (25 cm³). The resulting mixture was refluxed for 2 h, then filtered and allowed to stand at room temperature for 4 days. A white crystalline precipitate (**3**) formed, which was filtered off and vacuum dried. Yield: 18% (0.04 g). Found: C, 28.6; H, 3.9; S, 12.6. Calc. for C₂₄H₃₆S₄Hg₂Cl₄, C, 28.9; H, 3.6; S, 12.9%. ¹H NMR (400 MHz, CDCl₃), δ 1.20 (t, 6, --C<u>H</u>), 2.46 (q, S--C<u>H₂--</u>CH₃), 3.77 (s, 4, S--C<u>H₂--</u>CH₃), 7.19-7.27 (m, 14, Ph).

 $[{CuL^{3}Cl}_{2}]$ (4). CuCl₂·2H₂O (0.075 g, 0.44 mmol) dissolved in methanol (5 cm³) was added to a solution of L^3 (0.1 g, 0.44 mmol) in methanol (5 cm^3) . The green mixture was stirred for a few minutes, then H₃PO₂ (50% in water) was added dropwise until the solution became colourless. The resulting mixture was allowed to stand for 3 h. A colourless crystalline precipitate (4) formed, which was filtered off and vacuum dried. Yield: 84% (0.121 g). Found: C, 44.0; H, 5.6; S, 19.6. Calc. for C₁₂H₁₈S₂CuCl, C, 44.3 H, 5.6; S, 19.7%. ¹H NMR (400 MHz, CDCl₃), δ 1.20 (t, 6, --CH₃), 2.47 $(q, 4, S-CH_2-CH_3), 3.76 (s, 4, S-CH_2-CH_3),$ 7.18–7.28 (m, 14, Ph). ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃), δ 13.81 (--CH₃), 25.07 (S--CH₂--Ph), 35.15 (S-CH₂-Ph), 127.39, 128.40, 129.31, 139.06 (Ph).

Structure determinations

Data collection. Data were collected at room temperature on a CAD4-Enraf-Nonius diffractometer, using graphite-monochromated Mo- K_{α} radiation, $\lambda = 0.71073$, in $6\omega/10\theta$ scan mode for the structures (2), (3) and (4) with scan-width $(0.80 \pm 0.34 \text{ tan})$ $(\theta)^{\circ} + 25\%$ to determine the background, maximum measurement time 60 s; and in ω -scan mode for structure (1) with variable scan-width and maximum measurement time 120 s. Total changes in intensity of standard reflections during measurements were less than 4% and were not corrected. Absorption corrections were carried out on the basis of psi-scan data except for structure (4). The structures (2), (3) and (4) were solved using the Patterson function and difference Fourier syntheses (XTAL3.2¹¹ or MOLEN),¹² with neutral atomic form factors. Structure (1) was solved via direct methods and difference Fourier syntheses (XLENS¹³ and MOLEN).

Refinement details. All non hydrogen atoms were refined with anisotropic thermal parameters, except for structure (1), in which the Ag, S, N and O atoms were refined with anisotropic thermal parameters, while the carbon atoms were refined with isotropic thermal parameters, due to limited reflection data. In general, hydrogen atoms were placed in ideal calculated positions and were not refined. Fixed isotropic thermal parameters U(H) = 1.25U $(C_{\text{parent, ring}})$ or $U(H) = 1.5U(C_{\text{parent, chain}})$ were assigned to the hydrogen atoms. For structure (2) ring hydrogen atoms were placed in ideal calculated positions and CH₂ hydrogen positions were found from the difference Fourier map. A riding model was used for the ring hydrogen atoms during refinement, while CH₂ hydrogens were refined, all with fixed isotropic thermal parameters. The extinction coefficient was refined for (2), $\varepsilon = 2.897 \times 10^{-7}$. Weighting schemes used in refinement were $1/\sigma^2(F)$, which for the XTAL3.2 refinement is calculated with a modified σ : $\sigma^2(I) = \sigma^2(I)_{\text{diff}} + n\sigma^4(I)_{\text{diff}}$ n = 0.0004. Reflections with $I \ge 3\sigma(I)$ were used in the refinement of each structure.

Total number of parameters refined $(N_{\rm PR})$, number of reflections used in refinement $(N_{\rm o})$ and residual electron densities in the final difference Fouriers are given in Table 1.

	(1)	(2)	(3)	(4)
Formula	$C_{12}H_{16}S_2O_4NAg$	$C_{20}H_{18}S_2O_3NAg$	C ₂₄ H ₃₆ S ₄ Hg ₂ Cl ₄	C ₁₂ H ₁₈ S ₂ CuCl
М	410.25	492.36	995.80	325.40
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	Cmc2 ₁	$P2_1/n$	P1	$P2_1/c$
F(000)	824	992	472	668
$a(\mathbf{A})$	9.449(3)	10.605(7)	7.552(4)	7.475(2)
$b(\mathbf{A})$	20.082(4)	8.045(3)	9,493(4)	18.878(3)
$c(\mathbf{A})$	7.572(1)	24.236(19)	12.201(5)	10.717(3)
$\alpha(c)$	90	90	70.98(4)	90
$\beta(\mathbf{C})$	90	99.05(3)	77.99(4)	106.99(1)
?(^{°°})	90	90	88.07(3)	90
$U(Å^3)$	1437(1)	2042(2)	808.3(7)	1446.3(6)
$D_c(g \text{ cm}^{-3})$	1.90	1.60	2.04	1.49
Z	4	4	1	4
Specimen size (mm)	$0.10 \times 0.10 \times 0.05$	$0.27 \times 0.65 \times 0.15$	$0.37 \times 0.23 \times 0.20$	$0.37 \times 0.20 \times 0.09$
$\mu_{\rm Ma}(\rm cm^{-1})$	16.8	11.9	100.9	19.6
2θ	60.8	50	50	50
Reflection range	$0 \le h \le 13$	$-12 \le h \le 12$	$-8 \le h \le 8$	$-8 \le h \le 8$
	$0 \le k \le 28$	$0 \le k \le 9$	$-11 \le k \le 11$	$0 \le k \le 22$
	$0 \le 1 \le 10$	$0 \le 1 \le 28$	$0 \le 1 \le 14$	$0 \le 1 \le 12$
Unique reflections	1225	3964	2988	2684
N	603	2573	2696	1876
$T_{\rm max}(\%)/T_{\rm max}(\%)$	99 77/91 66	99 71/93 39	98.81/76.25	No correction
$N_{\rm DD}$	71	299	154	145
Redidual electron	/ L	<i>L</i> //	1.5 1	115
density ($\mathbf{e} \cdot \mathbf{A}^{-3}$)	0.55	0.51	0.65	1.0
R	0.042	0.033	0.023	0.040
		0.000	0.040	0.010

Table 1. Crystal data for compounds $[{AgL^1(NO_3)}_{x}]$ (1), $[{AgL^2(NO_3)}_{x}]$ (2), $[{HgL^3Cl_2}_{3}]$ (3) and $[{CuL^3Cl}_{x}]$ (4)

RESULTS AND DISCUSSION

Synthesis of the complexes

Silver(I) complexes of the L¹ and L² ligands were synthesized by mixing the appropriate ligand with AgNO₃ in the dark using methanol as a solvent. The mercury(II) complex of L³ was prepared *via* a similar method using HgCl₂ as the starting material in an HCl medium to avoid the hydrolysis of Hg^{II}. Copper(I) complex of L³ ligand was obtained from CuCl₂·2H₂O using H₃PO₂ as a reducing agent.

Structures of compound (1) and (2)

The single-crystal X-ray structure determination reveals that compounds (1) and (2) are polymeric complexes. Figures 1 and 2 show a portion of each polymer, respectively. Table 2 lists important bond distances and angles for compound (1), and Table 3 for compound (2). In both compounds the basic repeat unit includes a ligand, a nitrate anion and a silver(I) cation, and the polymers may be described as linear chains of alternating silver(I) cations and bridging ligands bonded through the sulfur atoms. In both silver structures the nitrate anion retains coordination to the metal atom, as observed in other polymeric silver coordination complexes with sulfur and nitrate ligands.¹⁴

The structure (1) is non centrosymmetric, space group Cmc2₁. The polymer chain is propagated parallel to the *a* axis *via* reflection operations, with the plane of the nitrate group lying perpendicular to the chain. The Ag atom and nitrate group lie on the mirror plane 0, *y*, *z* and the central atoms of the ligand, O(1), C(5) and C(7) lie on the mirror plane 1/2, *y*, *z*. Each silver(I) atom is bound to two symmetry-related sulfur atoms from different ligands units [Ag—S distances of 2.487(2) Å and



Fig. 1. Crystal structure and atom numbering scheme of the compound (1) projected along the *c* axis. Hydrogens are omitted for clarity.



Fig. 2. Crystal structure and atom numbering scheme of the compound (2) projected along the *b* axis. Hydrogens are omitted for clarity.

Table 2.	Bond	distances	(Å) and	selected	angles	([•]) with	their	e.s.d.
		in parenth	eses for	$[{AgL^1(l)}]$	NO_3) $\}_{\infty}$] (1)		

Ag—S	2.487(2)	C(1) - C(2)	1.489(1)
Ag-O(3)	2.400(8)	O(1) - C(2)	1.419(8)
O(2)—N	1.22(1)	C(3) - C(4)	1.49(1)
O(3)—N	1.24(1)	C(4) - C(5)	1.396(8)
O(4)—N	1.21(1)	C(6) - C(7)	1.39(1)
SC(1)	1.817(7)	C(4) - C(6)	1.401(9)
SC(3)	1.837(8)	AgO(2)	$2.68(1)^{a}$
S—Ag—S′	134.07(6)	O(2)NO(2	3) 119(1)
S	96.28(9)	O(2)—N—O(4	4) 120(1)
S-Ag-O(3)	110.76(5)	O(3)—N—O(4	4) 122(1)
Ag - S - C(1)	99.9(3)	S - C(1) - C(2)) 115.7(6)
Ag - S - C(3)	105.7(3)	O(1) - C(2) - O(2) -	C(1) 111.8(6)
C(1) - S - C(3)) 102.7(3)	C(2)-O(1)-O	C(2") 111.5(6)
AgO(2)N	89.3(6)	S-C(3)-C(4) 113.2(5)
Ag—O(3)—N	102.7(6)		

^{*a*} = Ag \cdots O(2) contact distance.

' = Symmetry operation -x, y, z.

" = Symmetry operation 1 - x, y, z.

S—Ag—S' angle of $134.07(6)^{\circ}$] and to the O(3) oxygen atom of the nitrate group [Ag—O(3) distance of 2.400(8) Å and S—Ag—O(3) angle of

110.76(5)^a]. In addition, a Ag-O(2) intramolecular contact of 2.681(10) Å is observed, which is longer than the sum of Ag and O ionic radii (2.55

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AgO(1)	2.757(4)		S(2)—C(11)1.767(4)	
Ag-O(2)	2.751(4)		O(1)—N(1) 1.221(5)	
Ag - S(1)	2.519(1)		O(2) - N(2) 1.212(5)	
Ag-S(2)	2.497(1)		O(3)—N(1) 1.193(5)	
S(1) - C(1)	1.833(5)		C(1) - C(2) 1.501(6)	
S(1)-C(21))1.776(4)		C(6)—C(7) 1.387(5)	
S(2)C(8)	1.822(5)		Ag-O(2') 2.490(4)	
O(1)—Ag—	-O(2)	44.1(1)	Ag - S(2) - C(8)	103.9(1)
O(1)—Ag—	-O(2')	69.8(1)	Ag - S(2) - C(11)	107.7(1)
O(2)Ag	-O(2′)	113.8(1)	Ag-O(1)-N(1)	97.6(3)
O(1)-Ag-	- S (1)	96.85(8)	Ag-O(2)-Ag'	137.4(2)
O(1)-Ag-	-S(2)	107.83(8)	Ag-O(2)-N(1)	98.1(3)
O(2')—Ag-	-S(1)	92.52(9)	O(2) - Ag - S(1)	96.77(8)
O(2')Ag	-S(2)	110.64(9)	O(2)—Ag— $S(2)$	90.34(8)
Ag—S(1)—	C (1)	102.8(1)	S(1)—Ag— $S(2)$	150.59(4)
Ag—S(1)—	C(21)	108.1(1)	Ag-O(2')N(1')	113.4(3)

Table 3. Selected bond distances (Å) and angles (²) with their e.s.d. in parentheses for $[{AgL^2(NO)_3)}_{\infty}]$ (2)

' = Symmetry operation 0.5 - x, y - 0.5, 0.5 - z.

Å).¹⁵ There are no interchain Ag—O contacts less than 3.50 Å.

The coordination geometry of silver(I) can be considered as distorted trigonal planar. The distortion of the trigonal planar geometry could be attributed to a weak Ag—O(2) interaction [2.68 (1) Å], forcing the O(3) oxygen atom out of the plane S—Ag—S'.

Structure of (2) conforms to the centrosymmetric space group $P2_1/n$ and the cell contains pairs of polymer chains that are related by 21 screw operations. The polymer chains are propagated by unit cell translations parallel to the *a* axis, with the nitrate groups lying tilted with respect to the axis and linked to neighbouring chains by long Ag-O(1) and Ag—O(2) contacts [2.757(4) and 2.751(4)] Å, respectively]. Silver(I) atoms are bonded to two sulfur atoms from two different ligands units [Ag-S(1) 2.519(1) Å, Ag-S(2) 2.497(1) Å and S(1)—Ag—S(2) 150.59(4)°] and to the O(2') oxygen atom of the vicinal nitrate group [Ag-O(2')]2.490(4) Å]. The coordination polyhedra of silver(I) is similar to that found in the structure of compound (1). It could also be considered as trigonal planar distorted by a weak bidentate nitrate ion interaction. In this case, the weakly bonded O(2) oxygen atom deviates 1.51 Å from the plane defined by sulfur and silver atoms.

The structures of silver nitrate complexes with the dithioethers presented here and those in the literature illustrate the flexible coordination characteristics of silver(I), the nitrate group and the dithioether ligands.¹⁶ Examples of coordination numbers 3–5 are observed for silver with Ag—S distances varying from 2.45 to 2.69 Å and Ag—ONO₂ distances varying considerably (2.33-2.79 Å). The nitrate anion coordinates in the unidentate or bidentate fashion, and can act as a bridge between silver(I) atoms. More important is the capability of the dithioethers to complex as unidentate of chelating ligands and as bridges. When acting as bridging ligands, coordination may occur through two or more different sulfur atoms of the ligand, or a single sulfur atom may bridge two silver atoms. These characteristics provide for a considerable variety and complexity of molecular structure.

Structure of compound (3)

The molecular structure of this compound is shown in Fig. 3. Selected bond distances and angles are listed in Table 4. The molecule is a dimeric complex, the halves being related by the centre of symmetry. Each Hg atom is bound to two bridging chlorine atoms [distances: 2.713(2) and 2.714(2) Å for Hg-Cl(2) and Hg-Cl(2'), respectively], one terminal chlorine atom [Hg-Cl(1); 2.391(2) Å] and one sulfur atom from the ligand [Hg-S(1)]; 2.499(2) Å]. The two Hg and the two bridging Cl atoms are in a nearly square-planar arrangement [angles; 89.85(5) and 90.15(5)° for Cl(2')-Hg-Cl(2) and Hg—Cl(2)—Hg', respectively]. The wide Cl(1)-Hg-S(1) angle of $157.47(5)^{\circ}$ is intermediate between a linear and trigonal geometry, suggesting that the preferred linear coordination of the strongly bonding Cl(1) and S(1) about mer-



Fig. 3. Perspective view and atom numbering scheme for the compound (3) in the form of ORTEP drawing. Thermal ellipsoids are drawn with surfaces at the 50% probability level.

Hg—Cl(1)	2.391(2)	C(1)C(6)	1.384(8)
Hg—Cl(2)	2.713(2)	C(1) - C(7)	1.516(9)
HgS(1)	2.499(2)	C(2)—C(3)	1.378(9)
HgCl(2')	2.714(1)	C(3)—C(4)	1.400(9)
S(1)C(7)	1.822(6)	C(3)—C(10)	1.498(7)
S(1)C(8)	1.824(5)	C(4) - C(5)	1.390(8)
S(2)—C(10)	1.809(6)	C(5)C(6)	1.37(1)
S(2)—C(11)	1.826(8)	C(8)C(9)	1.510(9)
C(1)—C(2)	1.375(7)	C(11)C(12)	1.47(1)
Cl(1)HgC	1(2) 97.83(6)	Hg - S(1) - C(3)	8) 107.2(2)
Cl(1)—Hg—S	(2) 157.47(5)	C(7)—S(1)—C	2(8) 100.5(3)
Cl(1)-Hg-C	1(2') 99.46(6)	C(10)-S(2)	C(11) 100.0(3)
Cl(2)—Hg—S	(1) 99.43(6)	S(1)—C(7)—C	C(1) = 111.1(4)
Cl(2)-Hg-C	1(2') 89.85(5)	S(1)-C(8)-C	C(9) 109.6(4)
S(1)-Hg-Cl	(2') 94.96(6)	S(2)C(10)	C(3) 114.3(4)
Hg-Cl(2)-H	(g′ 90.15(5)	S(2)-C(11)-	C(12) 111.9(6)
HgC(7) 101.1(2)		

Table 4. Bond distances (Å) and selected angles () with their e.s.d. in parentheses for $[\{HgL^3Cl_2\}_2]$ (3)

cury(II) is severely distorted by the presence of the weakly coordinated Cl(2) atom. In contrast with the other structures involving this ligand [compounds (2) and (4)], the S(2)-ligand atom does not coordinate to the metal ion. The closest Hg \cdots S(2) contact being 3.193(2) Å.

Structure of compound (4)

The structure of this compound is shown in Fig. 4. Selected bond distances and angles are listed in Table 5. The L³ ligand bridges dimeric Cu— Cl₂—Cu' units to form chains. The Cl—Cu—L³ fragment of each chain is related by the symmetry operation $-x, \frac{1}{2}+y, \frac{1}{2}+z$. The two halves of each dimeric Cu—Cl₂—Cu' unit are related by a centre of symmetry, thus linking the chains to form a three-dimensional polymer. Each Cu atom has a distorted tetrahedral environment including two sulphur atoms of different L³ ligands [2.281(1) and 2.296(1) Å for Cu—S(1) and Cu—S(2), respectively] and two bridging chlorine atoms [2.355(2) and 2.414(1) Å for Cu—Cl and Cu—Cl', respectively]. The most severe distortions are found in the Cl—Cu—Cl' and S(1)—Cu—S(2) angles [98.98(5) and 117.25(5)[°], respectively].

CONCLUSIONS

Compounds (1), (2) and (4) are polymers in which the dithioether acts as a bridging ligand, regardless of the acyclic (L^2 and L^3) or macrocyclic (L^1) nature of the ligand. In the dimeric structure of compound (3) the L^3 ligand acts as a monodentate



Fig. 4. Perspective view and atom numbering scheme of the polymeric compound (4) in the form of ORTEP drawing. Thermal ellipsoids are drawn with surfaces at the 50% probability level.

Cu—Cl	2.355(2)	C(1)—C(6)	1.372(6)	
Cu—S(1)	2.281(1)	C(1) - C(7)	1.511(6)	
Cu—S(2)	2.296(1)	C(2)—C(3)	1.398(6)	
Cu—Cu′	3.0983(9)	C(3)—C(4)	1.380(6)	
Cu—Cl′	2.414(1)	C(3)—C(10)	1.489(6)	
S(1)—C(7)	1.808(5)	C(4)C(5)	1.376(7)	
S(1)—C(8)	1.810(9)	C(5)—C(6)	1.389(7)	
S(2)C(10)	1.822(5)	C(8)C(9)	1.37(1)	
S(2)—C(11)	1.815(5)	C(11)—C(12)	1.51(1)	
C(1)C(2)	1.390(6)			
Cl—Cu—S(1)	111.66(6)	Cu-S(1)-C(7	7) 106.1(2)
Cl—Cu—S(2)	107.39(5)	Cu-S(1)-C(8	3) 113.6(2)
ClCuCl'	98.98(5)	Cu-S(2)-C(1	0) 105.5(2)
S(1)-Cu-S(2	117.25(5)	Cu - S(2) - C(1)	1) 114.0(2)
S(1)— Cu — Cl	110.01(5)	C(7)—S(1)—C	(8) 105.1(3)
S(2)-Cu-Cl	109.99(6)	C(10)-S(2)-6	C(11) 100.9(3)
Cu—Cl—Cu′	81.02(5)			

Table 5. Bond distances (Å) and selected angles ([°]) with their e.s.d. in parentheses for [{CuL³Cl}_x] (4)

' = Symmetry operation -x, 0.5 + v, 0.5 - z.

donor. From these results it could be concluded that the *meta*-xylene-based dithioether ligands show poor chelating ability towards d^{10} ions as silver(I), mercury(II) or copper(I).

The selectivity towards silver(I) exhibited by these compounds acting a neutral ionophores in membrane-based ISE's devices suggested that they might behave as chelating ligands.⁷ This hypothesis seemed to be confirmed by the ¹H-NMR shift of the aromatic proton located between the two *meta*xylene substituents. The shift is observed in solutions containing different ratios of these ligands and a silver(I) salt.⁸ However, we have recently demonstrated that a single monothioether compound also shows the same selectivity towards silver(I) in ISE's devices,¹⁰ indicating that chelation is not essential in this specific recognition phenomenon. The structural results reported here confirm this conclusion. Chelation by these ligands is not favoured for complexes of Ag¹, Hg^{II} and Cu¹ in the solid state. Chelation may still occur in the solution within the membrane, but is not a critical pathway for the recognition mechanism. The ligands, nevertheless, are effective complexing agents and show good selectivity towards silver(I) in ISE devices.

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Supplementary material available—Listings of positional parameters for non hydrogen and hydrogen atoms, anisotropic thermal parameters, bond angles and torsion angles for non hydrogen atoms and bond lengths for hydrogen atoms (21 pages). Listing of observed and calculated structure factors (56 pages) can be obtained from the author on request.

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