Binuclear Copper(I) Complexes of a 24-Membered Macrocycle (L^1) derived from 2,5-Diformylthiophene and 3-Thiapentane-1,5-diamine. Crystal and Molecular Structure of $[Cu_2L^1(NCS)][ClO_4]$; a Unique Example of a Single End-to-end Bridging Thiocyanate between Copper(I) Atoms‡

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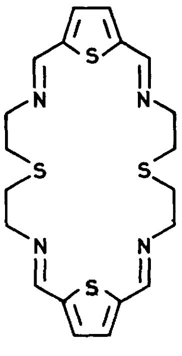
2,5-Diformylthiophene and 3-thiapentane-1,5-diamine in a metal-free non-template synthesis react to form a macrocycle L^1. A series of dicopper(I) complexes of L^1 have been prepared by reaction of copper salts with the macrocycle. Bridged complexes were isolated by adding an alkali-metal halide or pseudohalide to the reaction mixture. The dicopper(I) complexes were found to be remarkably stable, being unreactive towards both O_2 and CO. The crystal structure of one complex, $[Cu_2L^1(NCS)][ClO_4]$, has been determined. Crystals are triclinic, space group $P\bar{1}$, with $a = 9.735(8)$, $b = 11.967(9)$, $c = 13.859(11)$ Å, $\alpha = 76.0(1)$, $\beta = 104.4(1)$, $\gamma = 98.7(1)°$, and $Z = 2$. 2 024 Independent reflections above background were measured on a diffractometer and the structure refined to R 0.072. The two copper ions are bridged by a thiocyanate ion in an end-to-end 1,3-bridging mode. In addition each metal atom is bonded to two imine nitrogens and one thioether sulphur of the macrocycle and have very distorted tetrahedral environments.

We have previously reported[1] the preparation of a 24-membered Schiff-base macrocyclic ligand L^2, using Ag^I as a template. A series of dicopper(II) complexes were isolated and the structure of one, *viz.* $[Cu_2L^2(im)]^{3+}$ (im = imidazolate ion), was determined. The planar (conjugated) trimethine 'N_3' group in L^2 is well suited to co-ordinating Cu^{II},[2] binding to the three corners of an approximate square, the fourth corner being occupied, in the above case, by one of the nitrogens of the im.[1] The thioether sulphur atoms remain unco-ordinated. In the related macrocycle L^1, where the pyridine rings of L^2 have been replaced by thiophene rings, a significant change in the chemistry of the macrocycle was observed. The trimethine group in L^2 is less well adapted to co-ordination of Cu^I since, in order to achieve the favoured tetrahedral geometry for Cu^I, this N_3 unit must be considerably distorted from planarity.[2,3]

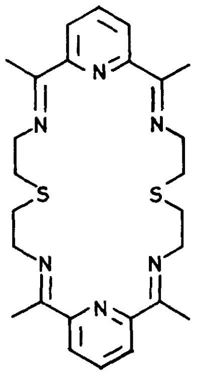
The L^1 macrocycle, however, forms a series of very stable complexes with Cu^I in which each metal centre has a distorted tetrahedral geometry. This macrocycle can be prepared in a metal-free Schiff-base condensation. Fenton and co-workers[4] have characterised a series of di(thiophene) containing macrocycles, all isolated by non-template procedures on reaction of 2,5-diformylthiophene with the corresponding diamines.

Since the macrocycle L^1 contains an 'N_4S_4' co-ordination sphere, including two thioether sulphur donor atoms, two thiophene sulphurs, and four imine nitrogen donors, it was expected that such an environment would stabilise the Cu^I ion. This proved to be the case.

These complexes contain a similar donor set to the Type 1 blue copper proteins, *e.g.* plastocyanin and azurin, in which the copper(II) has been reported to possess a distorted tetrahedral geometry, being bound to two nitrogen and two sulphur ligands.[5]



L^1



L^2

Experimental

Analytical data for all compounds are given in Table 1.

Preparation of L^1 *and the Disilver*(I) *and Dicopper*(I) *Complexes*.—The macrocycle L^1 was prepared by a (2 + 2) condensation of 2,5-diformylthiophene (0.7 g, 0.005 mol) and 3-thiapentane-1,5-diamine (0.6 g, 0.005 mol) in methanol (100 cm^3). After refluxing the solution for 5 min the product began to appear as a white solid. Refluxing was continued for 1 h. The resulting white solid was isolated and dried; yield *ca.* 70%.

No ^1H n.m.r. is available as the solid is very insoluble in most solvents. The parent ion peak, $P^+ = 448$, in the mass spectrum confirmed the presence of the (2 + 2) macrocycle.

$[Ag_2L^1(CH_3CN)(CH_3OH)][ClO_4]_2$ (**1**). This complex can be prepared by either (*a*) direct reaction of $AgClO_4$ with L^1 or (*b*) using Ag^I as a template for preparing L^1.

Method (*a*). The macrocycle L^1 (0.23 g, 5×10^{-4} mol) was stirred as a suspension in methanol–acetonitrile (2:1) (100 cm^3) and warmed to reflux. $AgClO_4$ (0.25 g, 1.2×10^{-3} mol) in methanol (20 cm^3) was then added and refluxing continued for 4 h. This solution was filtered and a white crystalline product isolated from the filtrate in 70% yield.

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‡ (6,19,27,28-Tetrathia-3,9,16,22-tetra-azatricyclo[22.2.1.$1^{11,14}$]octacosa-2,9,11,13,15,22,24,26-octaene-$N^3N^9S^6$: $N^{16}N^{22}S^{19}$)-μ-thiocyanato-NS-dicopper(I) perchlorate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Analytical, i.r., mass spectral, and electrical conductance data for the macrocycle and complexes

		Analysis (%)									
		Found			Calc.			I.r. bands (cm^{-1})			
Compound	Colour	C	H	N	C	H	N	ν(C=N)	ν(C≡N)	P^+	Λ/S cm^2 mol^{-1}
L^1	White	53.3	5.4	12.3	53.5	5.3	12.5	1 620		448	—
(**1**) $[Ag_2L^1(CH_3CN)(CH_3OH)][ClO_4]_2$	White	30.1	3.1	7.1	29.6	3.3	7.4	1 620	2 260		252
(**2**) $[Cu_2L^1(CH_3CN)_2][ClO_4]_2$	Red	32.6	3.6	9.6	32.9	3.7	9.6	1 620			264
(**3**) $[Cu_2L^1(NCS)][ClO_4]$	Red	34.7	3.6	9.3	34.4	3.3	9.5	1 615	2 090		168
(**4**) $[Cu_2L^1(N_3)][ClO_4]$	Brown	33.3	3.3	13.8	33.5	3.4	13.7	1 615	2 060*		156
(**5**) $[Cu_2L^1(NCSe)][ClO_4]$	Red-orange	32.4	3.2	9.0	32.3	3.1	9.0	1 615	2 090		149
(**6**) $[Cu_2L^1Cl][ClO_4]$	Yellow-brown	33.6	3.7	7.6	33.8	3.4	7.9	1 610			159
(**7**) $[Cu_2L^1Br][ClO_4]$	Yellow-brown	31.7	3.3	7.5	31.8	3.2	7.4	1 610			149
(**8**) $[Cu_2L^1I][ClO_4]$	Orange	30.3	2.9	7.2	30.0	3.3	7.5	1 610			133

* ν(N=N=N).

Table 2. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for $[Cu_2L^1(NCS)][ClO_4]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	952(2)	2 827(2)	3 173(1)	C(9)	4 774(15)	3 488(10)	3 424(12)
Cu(2)	4 024(2)	1 992(2)	6 788(2)	C(10)	3 829(18)	3 208(13)	2 522(11)
Cl(1)	0	0	0	N(11)	2 491(14)	2 909(10)	2 390(8)
O(11)	−1 145(95)	188(82)	464(63)	C(12)	1 794(18)	2 685(16)	1 407(12)
O(12)	1 134(53)	767(43)	46(34)	C(13)	787(21)	3 573(18)	849(13)
O(13)	−692(38)	173(28)	−1 176(27)	S(14)	−548(5)	3 690(5)	1 503(4)
O(14)	455(37)	−1 083(30)	181(25)	C(15)	−1 701(18)	2 399(18)	1 372(16)
Cl(2)	5 000	5 000	0	C(16)	−1 801(18)	1 608(18)	2 364(14)
O(21)	3 689(34)	4 991(24)	339(23)	N(17)	−405(13)	1 360(13)	2 990(10)
O(22)	5 971(37)	4 812(28)	973(26)	C(18)	−140(18)	318(15)	3 287(13)
O(23)	5 102(65)	4 813(44)	−806(40)	C(19)	1 101(17)	−105(15)	3 999(11)
O(24)	5 262(32)	6 419(27)	−210(22)	S(20)	2 145(4)	759(3)	4 791(3)
S(100)	457(4)	3 629(3)	4 338(3)	C(21)	3 282(17)	−265(11)	5 412(12)
C(100)	1 433(14)	2 993(12)	5 384(11)	C(22)	4 453(18)	−211(15)	6 249(16)
N(100)	2 171(12)	2 570(10)	6 142(9)	N(23)	4 811(14)	556(11)	6 749(11)
N(60)	354(39)	3 258(27)	7 873(24)	C(24)	6 049(18)	366(14)	7 596(14)
C(61)	1 850(32)	3 140(23)	8 386(20)	C(25)	5 648(21)	275(17)	8 598(14)
C(62)	−712(43)	2 973(33)	7 581(28)	S(26)	4 848(6)	1 486(6)	8 646(4)
C(4)	6 086(20)	3 617(20)	7 813(14)	C(27)	6 376(23)	2 540(19)	8 672(14)
N(5)	5 629(14)	3 333(11)	6 817(10)	C(41)	6 794(17)	4 228(13)	4 407(12)
C(6)	6 343(17)	3 916(14)	6 160(14)	C(42)	6 141(17)	4 007(12)	3 469(13)
C(7)	5 985(15)	3 822(11)	5 110(12)	C(51)	1 643(22)	−1 134(13)	4 242(14)
S(8)	4 316(4)	3 235(3)	4 575(3)	C(52)	2 827(20)	−1 201(16)	4 986(14)

Method (*b*). 2,5-Diformylthiophene (0.3 g, 2 × 10^{-3} mol) was dissolved in methanol (100 cm^3) and warmed to reflux whereupon $AgNO_3$ (0.35 g, 2 × 10^3 mol) was added and dissolved. 3-Thiapentane-1,5-diamine (0.22 g, 2.4 × 10^{-3} mol) in methanol (20 cm^3) was then added. The solution was refluxed for 3—4 h before addition of $NaClO_4$ (0.3 g, 2.5 × 10^{-3} mol) in methanol (20 cm^3). This solution was then filtered and concentrated on the rotary evaporator to 25 cm^3. A white solid was isolated in 50% yield.

$[Cu_2L^1(CH_3CN)_2][ClO_4]_2$ (**2**). This Cu^I complex was prepared by reacting $[Cu(CH_3CN)_4][ClO_4]$ or $Cu(ClO_4)_2 \cdot 6H_2O$ with L^1. To a stirred suspension of L^1 (0.23 g, 5 × 10^{-4} mol) in methanol–acetonitrile (2:1) (100 cm^3), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.4 g, 1.1 × 10^{-3} mol) was added as the solid and dissolved to give a dark green solution. This was refluxed for 4—5 h and then filtered; red cubic crystals formed (55% yield) on leaving the filtrate overnight.

$[Cu_2L^1X][ClO_4]$ [X = NCS (**3**), N_3 (**4**), NCSe (**5**), Cl (**6**), Br (**7**), *or* I (**8**)]. A similar procedure to the above was carried out; however NaX (0.05 g, 6 × 10^{-4} mol) was added to the solutions, giving an immediate colour change from green to red-orange. The mixtures were refluxed for 4—5 h before filtering. The filtrates yielded crystalline products (for colours see Table 1). In the case of $[Cu_2L^1(NCS)][ClO_4]$ (**3**), red equant crystals resulted which were suitable for a crystal-structure determination.

X-Ray Structure Determination of $[Cu_2L^1(NCS)][ClO_4]$ (**3**).—Crystals of $[Cu_2L^1(NCS)][ClO_4]$ were prepared as described above.

Crystal data. $C_{21}H_{24}ClCuN_5O_4S_5$, $M = 669.8$, triclinic, space group $P\bar{1}$, $a = 9.735(8)$, $b = 11.967(9)$, $c = 13.859(11)$ Å, $\alpha = 76.0(1)$, $\beta = 104.4(1)$, $\gamma = 98.7(1)°$, $U = 1\,510.5$ Å^3, $F(000) = 628$, $Z = 2$, $D_c = 1.33$ g cm^{-3}, μ(Mo-K_α) = 4.94 cm^{-1}, λ(Mo-K_α) = 0.7107 Å.

A crystal of approximate size 0.5 × 0.33 × 0.15 mm was mounted to rotate about the *a* axis on a Stoe Stadi-2 diffractometer and data collected *via* variable width ω scan. Cell dimensions were obtained by measuring high-angle reflections. Background counts were 20 s and a scan rate of 0.033° s^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. 5 312 Independent reflections with $2\theta < 50°$ were measured, of which 2 024 with $I > 3\sigma(I)$ were used in the subsequent refinement. The structure was determined by the usual heavy-atom methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in trigonal or tetrahedral positions and their positions refined. The structure was then refined by full-matrix least squares to R 0.072 (R' 0.073). The weighting scheme used was $w = 1/[\sigma^2(F) + 0.003F^2]$. All calculations were carried out with SHELX 76 [6] and some of our own programs on the Amdahl V7 computer at the University of Reading. Atomic positions are listed in Table 2 and the geometry of the metal co-ordination spheres is given in Table 3.

Other Physical Measurements.—Infrared spectra were measured as KBr discs and Nujol mulls using a Perkin-Elmer 598 spectrometer. ^{1}H N.m.r. spectra were recorded at room temperature in CD_3CN using a Bruker WM250 instrument. The mass spectrum of L^1 was recorded on an A.E.I. MS30 spectrometer. Electronic spectra were recorded as Nujol mulls and in CH_3CN at room temperature on a Perkin-Elmer SP700 spectrophotometer. Electrical conductances in CH_3CN solutions (10^{-3} mol dm^{-3}) at 25 °C were measured with a resistance–capacitance bridge between bright Pt electrodes in a cell of cell constant 0.037.

Table 3. Molecular dimensions in the metal co-ordination sphere; distances in Å, angles in degrees

Cu(1)–S(100)	2.243(5)	Cu(2)–N(100)	1.952(11)
Cu(1)–N(11)	2.036(14)	Cu(2)–N(5)	2.064(12)
Cu(1)–S(14)	2.485(5)	Cu(2)–N(23)	2.001(15)
Cu(1)–N(17)	2.059(14)	Cu(2)–S(26)	2.451(5)
S(100)–Cu(1)–N(11)	140.66(37)	N(100)–Cu(2)–N(5)	111.07(49)
S(100)–Cu(1)–S(14)	106.52(19)	N(100)–Cu(2)–N(23)	130.9(5)
N(11)–Cu(1)–S(14)	85.97(33)	N(5)–Cu(2)–N(23)	109.3(5)
S(100)–Cu(1)–N(17)	110.82(46)	N(100)–Cu(2)–S(26)	121.92(45)
N(11)–Cu(1)–N(17)	107.6(5)	N(5)–Cu(2)–S(26)	86.36(38)
S(14)–Cu(1)–N(17)	83.36(35)	N(23)–Cu(2)–S(26)	87.01(45)
Bridge dimensions			
S(100)–C(100)	1.607(13)	Cu(1)–S(100)–C(100)	102.7(6)
C(100)–N(100)	1.164(16)	S(100)–C(100)–N(100)	177.6(12)
		Cu(2)–N(100)–C(100)	146.1(13)

Results and Discussion

On reaction of equimolar quantities of 2,5-diformylthiophene and 3-thiapentane-1,5-diamine in methanol, the (2 + 2) condensation product resulted, as confirmed by mass spectroscopy ($P^+ = 448$). This is probably the preferred product due to its insolubility in solution. There were no bands at 1 700 or ~3 300 cm^{-1} in the i.r. spectrum which might indicate incomplete condensation. The macrocycle was also prepared with two Ag^I ions acting as templates, yielding the disilver(I) complex of L^1. The yield in this case however was not as high as that in the metal-free synthesis. The success of the metal-free synthesis may be due to the low solubility of the macrocycle compared to other oligomeric products. The macrocyclic product was confirmed by elemental analysis and the i.r. spectrum (Table 1) which shows a band at 1 620 cm^{-1} characteristic of ν(C=N).

The dicopper(I) complex $[Cu_2L^1(CH_3CN)_2][ClO_4]_2$ (**2**) was prepared by reaction of $[Cu(CH_3CN)_4][ClO_4]$ or $Cu(ClO_4)_2 \cdot 6H_2O$ with L^1 in CH_3CN–CH_3OH. The other dicopper(I) complexes of L^1 were prepared by adding the corresponding alkali-metal halide or pseudohalide salt to the above solution. In all cases the products were the dicopper(I) salts of L^1 and were air-stable. Although these reactions were all performed in the air, no Cu^{II} salts of L^1 were isolated. The only other metal to form a complex with the macrocycle was Ag^I which yielded $[Ag_2L^1(CH_3CN)(CH_3OH)][ClO_4]_2$. This was isolated either by using Ag^I as a template or by direct reaction of $AgClO_4$ with a suspension of L^1 in CH_3OH–CH_3CN. In all the reactions with this macrocycle it was gradually drawn into solution over a period of several hours refluxing in the presence of the Ag^I and Cu^I metal ions. Any unreacted macrocycle was then removed by filtration and the filtrate yielded the pure products (Table 1).

Treatment of L^1 with other metal ions including the first-row transition metals Mn^{II}, Fe^{II}, Fe^{III}, Co^{II}, Ni^{II}, Zn^{II}, as well as Pd^{II} and Pb^{II} gave no reaction, the macrocycle apparently being quite selective for Cu and Ag in the +1 oxidation state.

Infrared Spectra.—Infrared data (Table 1) indicated that the macrocycle was still present intact in the complexes. The perchlorate peaks ν_3 and ν_4 at ~1 090 and ~625 cm^{-1} respectively, for the complexes in Table 1, were unsplit suggesting that the $[ClO_4]^-$ ion is unco-ordinated in all the complexes prepared.

The dicopper(I) complex (**2**) contains two CH_3CN molecules which are probably terminally bound through the nitrogen, similarly to a previously reported complex.[7] The solid-state i.r. spectrum shows two weak peaks due to $\nu_{asym.}$(C≡N), the more intense occurring at 2 260 cm^{-1}. The absence of ν(C≡N) has been noted in the i.r. spectrum of a rhenium complex containing terminally bound CH_3CN.[8] In the thiocyanate and seleno-

Table 4. Electronic and proton n.m.r. spectral data for the complexes

	10^{-3} ν/cm^{-1} *					Proton n.m.r. (δ/p.p.m.)			
Compound	CH_3CN solution			Solid state		H^1	H^2	H^3	H^4
(**1**) $[Ag_2L^1(CH_3CN)(CH_3OH)][ClO_4]_2$						8.25(s)	9.34(s)	4.39(t)	3.75(t)
(**2**) $[Cu_2L^1(CH_3CN)_2][ClO_4]_2$	31.3(18)	26.0 (sh)		31.0	25.5 (sh)	7.55(s)	8.65(s)	3.65(t)	2.85(t)
(**3**) $[Cu_2L^1(NCS)][ClO_4]$	31.1(17)	25.7 (sh)			26.3 (sh)	7.59(s)	8.63(s)	3.68(t)	3.06(t)
(**4**) $[Cu_2L^1(N_3)][ClO_4]$	31.5(25)	28.0 (sh)	27.0 (sh)	30.8	27.6 (sh)	7.77(s)	8.85(s)	3.89(t)	2.10(t)
(**5**) $[Cu_2L^1(NCSe)][ClO_4]$		28.0 (sh)			26.8 (sh)				
(**6**) $[Cu_2L^1Cl][ClO_4]$		26.6 (sh)			26.0 (sh)	8.30(s)	9.30(s)	4.38(t)	3.58(t)
(**7**) $[Cu_2L^1Br][ClO_4]$	30.0(20)	27.1 (sh)			27.3 (sh)				
(**8**) $[Cu_2L^1I][ClO_4]$		27.7 (sh)			27.5 (sh)				

* 10^{-3} ε/dm^3 mol^{-1} cm^{-1} given in parentheses; sh = shoulder peak.

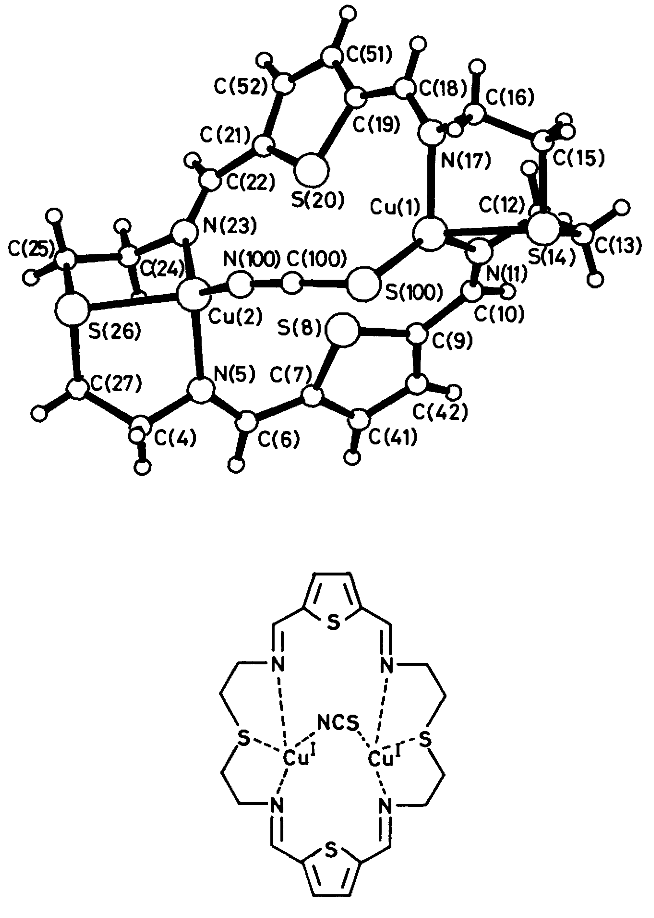

Figure 1. Crystal structure and graphic representation of the $[Cu_2L^1(NCS)]^+$ cation

cyanate complexes (3) and (5) (Table 1), both $\nu_{asym.}$ bands occur at 2 090 cm^{-1}. In the thiocyanate complex (3), this is due to the μ-1,3-bridged NCS^- (Figure 1). It is likely that the $SeCN^-$ ion also adopts this μ-1,3-bridging mode in (5) as does N_3^- in (4). The spectrum of (4) is similar to that of a μ-1,3-bridging azide structure which has been established by *X*-ray crystallography.[9]

Electronic Spectra.—The solid-state and CH_3CN solution electronic spectra (Table 4) are quite similar suggesting that the solid-state structures are retained in solution. Thus the mono-bridged halide and three-atom bridged pseudohalide structures remain undissociated on dissolving in CH_3CN at room temperature. The highest energy band is assigned as a ligand based π–π^* transition. The lower energy bands are assigned as metal-to-ligand $d\pi$–$p\pi^*$ charge-transfer transitions and are responsible for the colour of the complexes.

The two diperchlorate complexes of Ag^I and Cu^I [*i.e.* (1) and (2)] with conductivities of 252 and 264 S cm^2 mol^{-1} respectively (Table 1) are 2:1 electrolytes. However the conductivities (Table 1) of the other complexes containing halide or pseudohalide bridges are characteristic of 1:1 electrolytes, consistent with the retention of the bridging anions in CH_3CN solution.

^1H *N.M.R. Spectra.*—The results of the ^1H n.m.r. spectra for the complexes are given in Table 4 and the spectrum of $[Cu_2L^1Cl][ClO_4]$ (6) is shown in Figure 2. The spectra for all the complexes are consistent with the macrocyclic structure being retained in CD_3CN solution. The macrocycle itself is insoluble.

The Cu^I complexes of L^1 were all found to be very unreactive to CO and O_2. Gas-uptake studies on the complexes in CH_3CN and dimethylformamide (dmf) showed no consumption of gas. However, over a period of several days exposure to air the yellow dmf solution of $[Cu_2L^1(CH_3CN)_2][ClO_4]_2$ turned green indicating some interaction with oxygen. The reason for the lack of reactivity with O_2 and CO is attributed to the stable

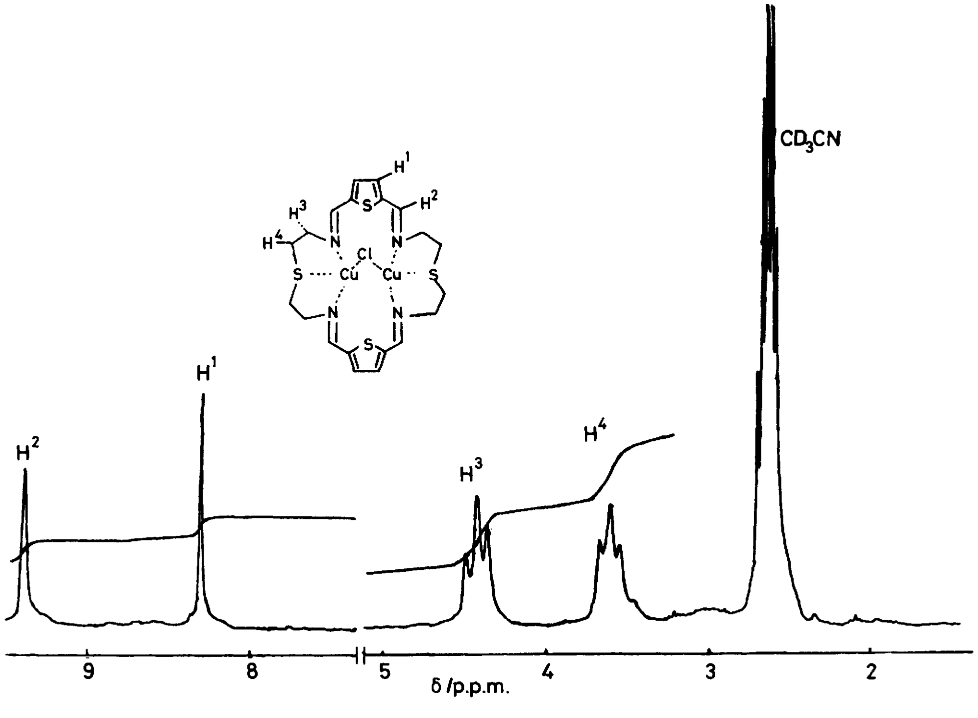

Figure 2. The ^1H n.m.r. spectrum of $[Cu_2L^1Cl][ClO_4]$ (6) in CD_3CN at 293 K

four-co-ordinate structures assigned to the dicopper(I) complexes. The halide and pseudohalides are particularly stable.

Discussion of the Structure of $[Cu_2L^1(NCS)][ClO_4]$ (**3**).—The structure of complex (**3**) is shown in Figure 1 together with the atomic numbering system. The copper atoms are enclosed within the macrocycle, each being bound to two imine nitrogens and a thioether sulphur of the macrocycle. In addition the two metal atoms are bridged by a thiocyanate ion in an end-to-end (μ-1,3) bridging mode giving each metal atom a non-equivalent four-co-ordinate structure. The Cu(1) atom has a 'N_2S_2' co-ordination environment with bond lengths of Cu(1)–S(100) 2.243(5), Cu(1)–N(11) 2.036(14), Cu(1)–N(17) 2.059(14), and Cu(1)–S(14) 2.485(5) Å. The geometry is highly distorted from tetrahedral with angles ranging from 140.7(4)° for S(100)–Cu(1)–N(11) to 83.4(3)° for S(14)–Cu(1)–N(17). The Cu(1)–S(100) distance is relatively short.

In a survey of Cu^I–SCN structures from the Cambridge Data Centre, we found the shortest Cu–S distances were 2.232 Å in polymeric $[\{Cu(dmp)(\mu\text{-}SCN)\}_n]$ (dmp = 2,6-dimethylpyridine) and 2.291 Å in polymeric $[\{Cu(C_9H_7N)(\mu\text{-}SCN)\}_n]$.[10] In all the other compounds the Cu—S distances were greater than 2.30 Å. This data search also shows that there are no precedents for the single thiocyanate bridge in the present structure. All other structures have one or more thiocyanate ion per copper atom.

One reason for this unique structure is presumably that the steric constraints of the macrocycle preclude a di-μ-thiocyanate bridge. From the Cambridge Data Centre files, we found that the metal–metal distance in such structures ranges from 5.3 to 5.8 Å, rather more than the distance found in (**3**). Another reason may be that the stereochemical requirements of the Cu^I atoms are satisfied by the distorted tetrahedral environment. A di-μ-thiocyanate bridge would require either a five-co-ordinate structure which has been observed for copper(I),[2,11] or a weakening of the Cu–S(14) thioether interaction. The steric constraints of this particular macrocycle are indicated by the range of angles around Cu(1) and Cu(2).

The Cu(1) atom has an 'N_2S_2' co-ordination environment although the geometry is highly distorted from tetrahedral. In contrast Cu(2) has 'N_3S' co-ordination and the distortion from ideal tetrahedral is not quite as large as that around Cu(1). Bond lengths are Cu(2)–N(100) 1.952(11), Cu(2)–N(5) 2.064(12), Cu(2)–N(23) 2.001(15), and Cu–S(26) 2.451(5) Å. The angles range from 130.9(5)° for N(100)–Cu(2)–N(23) to 86.4(4)° for N(5)–Cu(2)–S(26).

The strain in the macrocycle is responsible for the distortion from tetrahedral geometry for each metal centre. The thiocyanate bridge sits in a skew position to favour the correct geometry for each end of the bridge. Thus for the sulphur end the Cu–SCN bond, which is particularly short, has a bond angle Cu(1)–S(100)–C(100) of 102.7(6)°, slightly distorted from the expected 90°, whereas the Cu(2)–N(100) bond length of 1.952(11) Å which is also short has an associated Cu(2)–N(100)–C(100) bond angle of 146.1(13)° which is quite distorted from the more usual linear bonding at this end of the thiocyanate. A survey of such structures in the Cambridge Data Centre files showed up 80 examples from 38 structures with an average angle of 160.8°. This is yet another indication of the strain that the L^1 macrocycle imposes on the metal centres.

The Cu(1) $\cdots$ Cu(2) distance of 5.07 Å is shorter than that in the imidazolate bridged dicopper(II) complex of L^2 (5.87 Å).[1] Complex (**3**) (Figure 1) has a Cu $\cdots$ Cu vector perpendicular to that in $[Cu_2L^2(im)]^{3+}$.

Thus for the L^2 macrocycle Cu^{II} co-ordinates to the 'N_3' donor set of the trimethine group rather than to the thioether sulphurs. By contrast the thiophene sulphurs of the L^1 macrocycle apparently do not co-ordinate to the Cu^I metal atoms [Cu(1) $\cdots$ S(8) 3.40, Cu(1) $\cdots$ S(20) 3.06, Cu(2) $\cdots$ S(8) 3.13, and Cu(2) $\cdot\cdot$ S(20) 3.44 Å], although some weak interaction cannot be ruled out particularly for the two shorter distances. Indeed a study of the angles around Cu(1) and Cu(2) indicates that there is room for such a weak interaction. This can be observed by examining the structure in Figure 1. Further evidence of such an interaction is derived from the ability of L^1 to stabilise the Cu^I oxidation state, no Cu^{II} complexes being isolated. This contrasts with the pyridine containing macrocycle L^2 which does stabilise the Cu^{II} oxidation state.[1] Despite the poor co-ordination properties of thiophene sulphur,[12] the two thiophene rings present in L^1 are thought to have an important influence on the properties of L^1 in comparison with the influence of pyridine in L^2. The presence of the five-membered rings is most likely to be responsible for the selectivity displayed by L^1 in binding only the Cu^I and Ag^I metal ions.

There is one perchlorate per cation. This is disordered over two positions. The two alternative chlorine atoms both occupy centres of symmetry and disordered models of oxygen atoms were refined. There are no intermolecular distances of note.

The other complexes of L^1 probably also have distorted tetrahedral structures around the metal ions similar to that shown in Figure 1. Each metal ion is co-ordinated to the tridentate N_2S donors of L^1 and to one other bridging anion or terminally N-bound CH_3CN. The pseudohalide complexes most probably contain azide [(**4**)] and selenocyanate [(**5**)] in the μ-1,3-bridging mode in a similar manner to (**3**) in Figure 1. The halide complexes (**6**), (**7**), and (**8**) are proposed to contain one-atom bridges between the two Cu^I ions, the flexibility of L^1 enabling the metal ions to be close enough to accommodate a one-atom bridge.

We have carried out molecular mechanics calculations on these postulated structures using our published method.[13] Using equivalent parameters to those reported in ref. 13, we found that the steric energy for the present structure was 33.6 kcal mol^{-1}. An alternative structure with a 1,1-NCS bridge refined to a steric energy of 44.8 kcal mol^{-1}. We also calculated the energy of the proposed halide bridge and found that this structure was viable with a steric energy (for chlorine) of 39.6 kcal mol^{-1}.

Conclusions

The macrocycle L^1 has been prepared in a metal-free synthesis. The macrocycle, which contains eight potential donor atoms (4 S and 4 N), was expected to bind a series of transition metals and main group metals forming both mono- and bi-nuclear complexes. However, we were unable to isolate any other metal complexes of L^1 other than the disilver(I) and dicopper(I) complexes in Table 1. On reaction with other metal ions the free macrocycle was recovered.

Also significant was the reaction of L^1 with $Cu(ClO_4)_2\cdot 6H_2O$ which on refluxing always led to the reduced dicopper(I) complex. No Cu^{II} complexes could be isolated for L^1. The electrochemical properties of these complexes are currently under investigation. The value of the redox potential for the Cu^{II}–Cu^I couple for the complexes will be contrasted with that for Type I copper proteins.

The stability of the dicopper(I) complexes was demonstrated by the lack of reaction with both O_2 and CO in solution. This is a good indication that the stable tetrahedral structures proposed for the solids are retained in solution.

The selectivity of L^1 for Cu^I and Ag^I may be due to the presence of the thioether groups or the two thiophene rings. However since L^2 also contains the thioether groups and does not display the same selectivity,[1,14] it is most likely that the thiophene rings have a significant influence on the properties of the macrocycle.

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