The Synthesis, Properties, and the Crystal and Molecular Structures of Five-co-ordinate Copper(I) and Silver(I) Complexes of a Quinquedentate Macrocyclic Ligand having an 'N_3S_2' Donor Set

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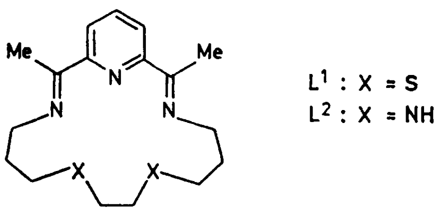
The 17-membered macrocyclic ligand L^1 containing the 'N_3S_2' donor set has been synthesised [and isolated as the silver(I) complex] by the template action of silver(I) salts on the cyclic Schiff-base condensation of 2,6-diacetylpyridine with 1,10-diamine-4,7-dithiadecane. The copper(II) ion was ineffective as a template for the synthesis. However, copper(II) complexes of L^1 could be obtained from $[AgL^1]^+$ *via* metal exchange (transmetallation). Sodium tetraphenylborate is a reducing agent for $[Cu^{II}L^1]^{2+}$, affording $[Cu^{I}L^1]^+$ in good yield. Possible mechanisms for the reducing action of $[BPh_4]^-$ are discussed. Hydrogenation of $[AgL^1]^+$ salts using $Na[BH_4]$ give the free reduced macrocycle RL^1 (*i.e.* L^1 + 4H) from which a new range of macrocyclic complexes may be obtained. Infrared and electronic spectra of the silver(I) and copper(I) complexes of L^1 are reported. The copper(I) complexes are unreactive to both O_2 and CO. Crystals of $[CuL^1][ClO_4]$ are orthorhombic with a = 6.844(7), b = 12.361(11), c = 24.072(21) Å, Z = 4, and space group $P2_12_12_1$. Crystals of $[AgL^1][BPh_4]$ are monoclinic with a = 13.132(11), b = 25.001(12), c = 12.479(12) Å, β = 105.7(1)°, Z = 4, and space group $P2_1/c$. The two structures were solved by Patterson and Fourier methods from 927 and 2 621 reflections above background measured by diffractometer and refined by full-matrix least squares to R 0.077 and 0.071 respectively. While the co-ordination geometry of both complexes is a distorted trigonal bipyramid there are marked differences in the macrocycle conformations in the two cases and, for the copper(I) complex, in the metal–nitrogen bond lengths. These are discussed in relation to the sizes of the two metal ions and of the macrocycle hole size.

IN comparison with the transition metals, little is known of the co-ordination chemistry of the d^{10} ions Cu^I and Ag^I in complexes of multidentate ligands.[1] We have previously described five-co-ordinate [2] (monomeric) and six-co-ordinate [3] (dimeric) structures for silver(I) complexes of two 'N_5' macrocycles. Louis *et al.*[4] reported distorted square-pyramidal structures for the complexes of two isomeric 'N_2S_2O' macrocycles with Ag[SCN], and Gagné *et al.*[5] have recently described a square-pyramidal CO adduct of a copper(I) complex of an 'N_4' macrocycle. A greater knowledge of the structural co-ordination chemistry of Cu^I, particularly in a nitrogen–sulphur ligand environment, is important in view of current interest in understanding the structure–function relationships of the 'blue' or 'type 1' copper proteins. Recent structural investigations of copper(II) plastocyanin [6] (from *Populus nigra Var. italica*) and of azurin [7] (from *Pseudomonas aeruginosa*) as well as of certain model compounds [8] point to a relationship between the unique properties [9] (redox potentials, electronic and e.s.r. spectra) of this class of copper protein and the occurrence of the metal atom in a low-symmetry (distorted tetrahedral) environment made up of both nitrogen (imidazole) and sulphur (mercaptide or thioether) donor atoms.

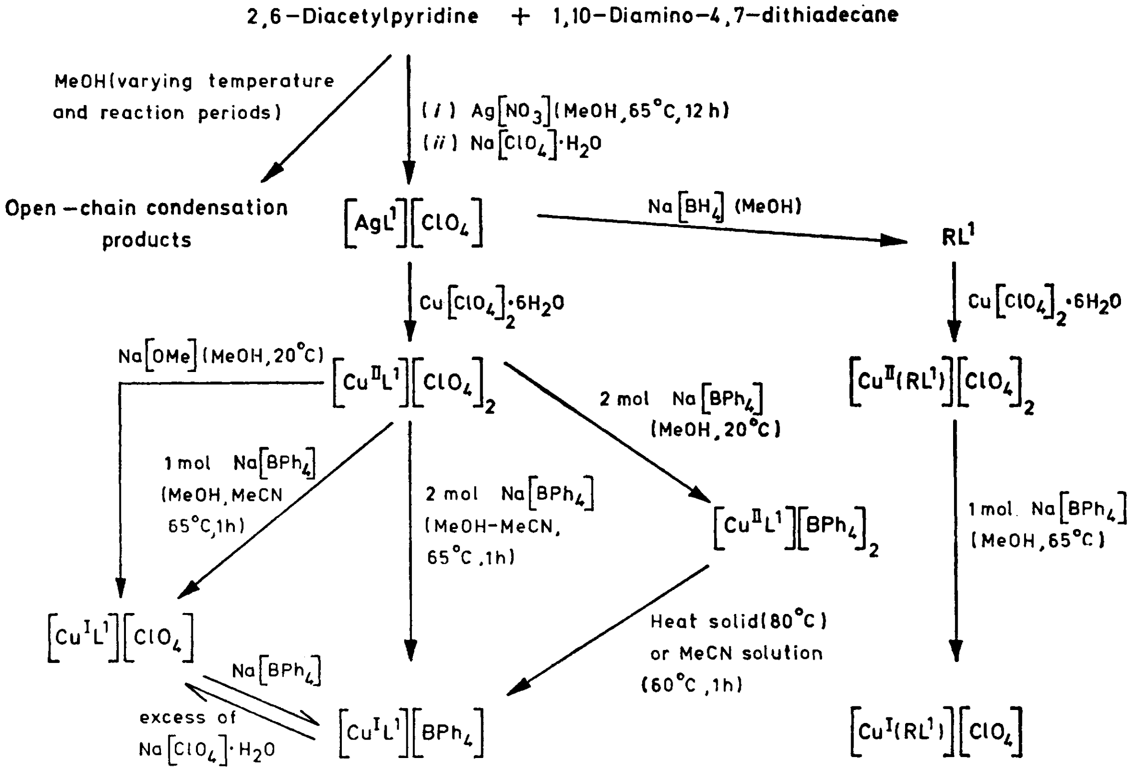
In this paper we describe the synthesis, structures, and some properties of copper(I) and silver(I) complexes of the potentially quinquedentate nitrogen–sulphur macrocycle L^1 {2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo[14.3.1]icosa-1(20),2,14,16,18-pentaene}, as part of a continuing investigation of the relationship between macrocycle size, flexibility, and the number and nature of the donor atoms, on the one hand, with the size and electronic configuration of metal ion on the other. This macrocycle appeared to us to be an appropriate choice of multidentate 'nitrogen–sulphur' ligand with which to further explore the co-ordination chemistry of Cu^I and Ag^I for two reasons. Firstly, being 17-membered it is sufficiently flexible to respond reasonably well to the stereochemical preferences of the central metal ion. This view is based on previous work on related 'N_5' macrocycles which showed that, in contrast to the 15- and 16-membered homologues, the 17-membered ring L^2 can adopt a variety of conformations while functioning as a quinquedentate ligand.[2,10-12] Secondly, there was the possibility that one or both of the sulphur atoms might not be used in co-ordination, as found for some transition-metal complexes of the same ligand.[13] Thus the denticity as well as the conformation of the macrocycle are potentially variable.



RESULTS

Synthesis of the Complexes.—The macrocycle L^1 was prepared by the template action of a salt (nitrate or perchlorate) of Ag^I in a '1 + 1' cyclic Schiff-base condensation of 2,6-diacetylpyridine with 1,10-diamino-4,7-dithiadecane in methanol (see Scheme 1 and Experimental section for details). The macrocycle was isolated as the complex $[AgL^1]X$ ($X = ClO_4^-$ or BPh_4^-) as yellow crystals in 65—70% yield. The template action of the Ag^I ion was demonstrated by the failure to effect cyclisation in the absence of a soluble silver(I) salt; under such conditions only oily or gummy, presumably oligomeric, products of indefinite composition were obtained. These gave broad, ill defined i.r. spectra indicating the presence of unreacted carbonyl and/or primary amine groups.

Copper(II) salts appear to be ineffective for the synthesis of L^1. The copper(I) complexes, which are the subject of this paper, were therefore prepared *via* a two-stage synthesis from the initially prepared complex $[AgL^1][ClO_4]$ involving metal exchange (transmetallation) with Cu^{II} followed by chemical reduction (Scheme 1). Treatment of $[AgL^1][ClO_4]$ with an excess of $Cu[ClO_4]_2{\cdot}6H_2O$ in hot MeOH quickly generated a deep blue colour from which crystals of the complex $[Cu^{II}L^1][ClO_4]_2$ were obtained.* Treatment of this complex with two equivalents of $Na[BPh_4]$ in MeOH at room temperature yielded green $[Cu^{II}L^1][BPh_4]_2$. During the preparation of this complex it was observed that if the reaction mixture was heated to reflux the initial green colour became dark brown. Reflux for 30 min followed by concentration afforded a dark brown crystalline material of stoicheiometry $[CuL^1][BPh_4]$ in 55% yield. This complex is diamagnetic and gave no e.s.r. signal. The i.r. spectrum (see later) is closely similar to that of $[AgL^1][BPh_4]$. It can therefore be formulated as a copper(I) complex of the unchanged macrocycle L^1. Subsequent experiment established that the use of not more than one equivalent of $Na[BPh_4]$ in the preparation affords the perchlorate salt $[Cu^IL^1][ClO_4]$. Moreover, $[Cu^{II}L^1][BPh_4]_2$ spontaneously converted to $[Cu^IL^1][BPh_4]$ in MeCN solution (*ca.* 1 day at 20 °C; *ca.* 1 h at 60 °C) and also in the solid state (*ca.* 2 h at 80 °C). In contrast, the complex $[Cu^{II}L^1][ClO_4]_2$ showed no tendency to undergo reduction. We conclude, therefore, that the tetraphenylborate anion is responsible for the reducing action. The mechanism of the reaction, which also occurs with several related copper(II) complexes and which affords a convenient synthetic route to copper(I) complexes, is currently under investigation. We note that Karlin *et al.*[14] have recently reported the preparation of a distorted tetrahedral copper(I) complex in *ca.* 30% yield of the 'N_2S_2' ligand bis[2-(ethylthio)ethyl][2-(2-pyridyl)ethyl]amine by treatment of the copper(II) complex in aqueous solution with $Na[BPh_4]$. No comment on possible mechanisms was made. It seems likely that a key step in the reduction of L^1 is a nucleophilic attack on the complex by Ph^- (or by OMe^- generated from Ph^- in MeOH solution) formed in a metal-assisted decomposition of $[BPh_4]^-$, this being followed by electron transfer to the Cu^{II} centre with accompanying formation of the phenyl (or methoxyl) radical. Significantly, the reduction can also be performed by the use of Na[OMe]. Furthermore, in an experiment in which the solid complex $[Cu^{II}L^1][BPh_4]_2$ was heated *in vacuo* to 100—120 °C a white sublimate was obtained in addition to the brown copper(I) species. The sublimate was identified as biphenyl by its melting point and i.r. and mass spectrum. We have not yet succeeded in identifying the boron-containing fragment.



Scheme 1

It is not possible at this stage to decide between a nucleophilic attack at the Cu^{II} centre or on the co-ordinated ligand, or both. In view of the known susceptibility of Schiff bases

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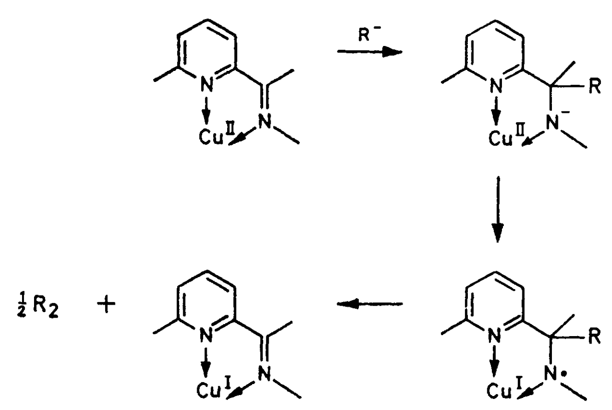
* The copper(II) complexes of L^1 will be described separately.[13] The *X*-ray structure of $[Cu^{II}L^1][ClO_4]_2$ has been solved; all five donor atoms of the macrocycle are bonded to the metal in a distorted square-pyramidal arrangement.

to hydrolysis [15] and to ROH adduct formation [10,16] a nucleophilic attack at the azomethine carbon atom seems a strong possibility (see Scheme 2). In favour of this mechanism as against one involving direct nucleophilic attack at the metal are our observations on the reaction of $[Cu^{II}(RL^1)][ClO_4]_2$ with $Na[BPh_4]$, where RL^1 is the reduced macrocycle formed by hydrogenation of the two azomethine linkages of L^1 (see below). Although this complex also developed an amber-brown colour on prolonged refluxing in MeOH with $Na[BPh_4]$ in the absence of air, the rate of development of the colour was much slower than with $[Cu^{II}L^1][ClO_4]_2$. A small amount of a light yellow solid could be isolated from these solutions, which on the basis of chemical analysis, i.r. spectra, and magnetic properties appears to be $[Cu^I(RL^1)][BPh_4]$. Since RL^1 lacks any imino bonds the nucleophilic attack in this case may be at the metal. Alternatively, it may occur at the pyridine ring as demonstrated by Gillard and co-workers [17] in the 'covalent hydration' and related reactions of metal complexes of 2,2'-bipyridyl and similar heterocyclic nitrogen ligands.



SCHEME 2

Characterisation of the Copper(I) *and Silver* (I) *Complexes*.—Analytical and selected physical data for the complexes $[ML^1]X$ [$M = Cu^I$ or Ag^I; $X = ClO_4^-$ or BPh_4^-] are given in Table 1. Infrared spectra indicate the presence of the imino (C=N) and pyridyl groups at *ca.* 1 630 and 1 400—1 600 cm^{-1} respectively. No absorption at *ca.* 1 700 cm^{-1} or at 3 200—3 400 cm^{-1} attributable to unreacted carbonyl or primary amine functions of the macrocycle precursors was observed. The i.r. spectra of the complexes of both metal ions are closely similar except for the variation attributable to the different anions. In the perchlorate the ν_3 and ν_4 modes of the ClO_4^- group occur as unsplit bands at *ca.* 1 090 cm^{-1} and *ca.* 620 cm^{-1}, consistent with its formulation as unco-ordinated anion. All the complexes show 1 : 1 electrolyte behaviour in acetonitrile and/or nitromethane solution, as does $[AgL^1][ClO_4]$ in water also (Table 1).

The highest mass peak in the mass spectrum of $[AgL^1][BPh_4]$ occurs at *m/e* 335 corresponding to the free macrocycle L^1. Confirmation of the presence of this macrocycle L^1 in the complexes was obtained by tetrahydroborate reduction of $[AgL^1][ClO_4]$ which on work-up yielded a yellow oil shown by chemical analysis, i.r. spectra, and mass spectra ($P^+ = 339$) to be the free reduced macrocycle (RL^1) formed by hydrogenation of the two azomethine linkages of L^1. Reaction of RL^1 with $Cu[ClO_4]_2{\cdot}6H_2O$ gave the complex $[Cu^{II}(RL^1)][ClO_4]_2$ (Table 1) in the i.r. spectrum of which the ν(C=N) mode is absent; instead, the spectrum shows single bands at 3 250—3 300 cm^{-1} and at 1 600—1 610 cm^{-1} attributable to the stretching and bending vibrations of the secondary NH groups.

Electronic spectra (6 000 to 30 000 cm^{-1}) of the complexes of L^1 were recorded in the solid state and in solution in MeCN. The spectra of the silver(I) complexes consist of a single band in the near u.v. at *ca.* 28 000 cm^{-1} which we assign to a Ag^I-to-macrocycle charge-transfer transition; it occurs as a shoulder on the side of a more intense higher energy band probably due to a transition of the co-ordinated macrocycle. The $[Cu^IL^1]^+$ complexes exhibit a strong band at 22 900 cm^{-1} in MeCN (ε 2 800 dm^3 mol^{-1} cm^{-1}). On the assumption that this is also due to a metal-to-ligand charge transfer its occurrence at a lower energy compared to that in the silver(I) complexes is consistent with the relative magnitudes of the M^I/M^{II} oxidation potentials [18] of the two metal ions.

TABLE 1

Analytical, magnetic, and electrical conductance data for the complexes

	Analysis (%)									
	Found			Calc.			Λ^a/S cm^2 mol^{-1}			
Complex	C	H	N	C	H	N	MeCN	$MeNO_2$	H_2O	$\mu_{eff.}{}^b$/ B.M.
$[AgL^1][ClO_4]$	37.5	4.9	7.8	37.6	4.6	7.7	159		120	Diamagnetic
$[AgL^1][BPh_4]$	64.1	6.1	5.6	64.6	6.0	5.5	116			Diamagnetic
$[Cu^IL^1][ClO_4]$	40.3	5.2	7.9	40.9	5.1	8.4	170	102		0.5
$[Cu^IL^1][BPh_4]$	68.2	6.6	6.0	68.5	6.3	5.9	125	75		0.5
$[Cu^{II}L^1][ClO_4]_2$	34.2	4.2	7.0	34.2	4.2	7.0	297	206		1.88
$[Cu^{II}L^1][BPh_4]_2$	75.0	6.4	4.2	75.2	6.3	4.1	222	163		1.74
$[Cu^I(RL^1)][BPh_4]$	68.0	6.9	5.9	68.1	6.8	5.9	120	75		0.7
$[Cu^{II}(RL^1)][ClO_4]_2$	33.8	4.9	6.8	33.9	4.9	7.0	285		209	1.95

[a] For 10^{-3} mol dm^{-3} solutions at 25 °C. [b] At 20 °C, corrected for diamagnetism of ligands; 1 B.M. = 9.274×10^{-24} A m^2.

In contrast to many other copper(I) complexes,[1,5] the $[Cu^IL^1]^+$ complex cation is unreactive towards carbon monoxide and dioxygen. Similarly, no reactivity towards halide ion was apparent. The lack of affinity of Cu^I towards these reagents may be related to the presence in the complex of five bonded donor atoms (see below) giving the metal ion an effective number of valence electrons of 18. The stability to oxidation is most probably associated with a stabilisation of the +1 oxidation state by the co-ordinated thioether groups.

Crystal Data.—(1) $[CuL^1][ClO_4]$, $C_{17}H_{25}ClCuN_3O_4S_2$, $M = 498.3$, Orthorhombic, $a = 6.844(7)$, $b = 12.361(11)$, $c = 24.072(21)$ Å, $U = 2\ 036.6$ Å^3, $F(000) = 1\ 032$, $D_m = 1.63(3)$, $Z = 4$, $D_c = 1.62$ g cm^{-3}, $\mu = 14.7$ cm^{-1}, space group

$P2_12_12_1$ from systematic absences $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$.

(2) [AgL^1][BPh$_4$], $C_{41}H_{45}AgBN_3S_2$, $M = 762.2$, Monoclinic, $a = 13.132(11)$, $b = 25.001(12)$, $c = 12.479(12)$ Å, $\beta = 105.7(1)°$, $U = 3\,944.2$ Å^3, $F(000) = 1\,584$, $D_m = 1.29(2)$, $Z = 4$, $D_c = 1.28$ g cm^{-3}, $\mu = 6.33$ cm^{-1}, space group $P2_1/c$ from systematic absences, $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$.

Crystals of both compounds were mounted on a General Electric XRD-5 diffractometer equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered Mo-K_α radiation was used. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken from plots of background against 2θ. For (1) a crystal of size 0.3 × 0.4 × 0.4 mm was selected and 1 231 independent reflections were measured with $2\theta < 40°$ of which 927 with $I > \sigma(I)$ were used in subsequent calculations. For (2), the crystal size was 0.7 × 0.3 × 0.5 mm and 3 465 independent reflections were measured with $2\theta < 40°$ of which 2 621 with $I > 2\sigma(I)$ were used. Neither extinction not absorption corrections were applied. Both structures were determined by normal Patterson and Fourier techniques. In (1) the copper, sulphur, chlorine, and oxygen atoms were refined anisotropically and carbon and nitrogen atoms isotropically. Hydrogen atoms were fixed in tetrahedral or trigonal positions and their thermal parameters only were refined. Both sets of methyl hydrogen atoms refined satisfactorily. The perchlorate oxygen atoms were highly anisotropic and we attempted to account for this *via* some form of disorder but without success. The structure was refined using SHELX '76 [19] to R 0.077. For (2) all atoms except hydrogen were given anisotropic thermal parameters. The hydrogen atoms were fixed in tetrahedral or trigonal positions but their thermal parameters were not refined. The methyl hydrogen atoms were not included. The structure was refined using '*X*-RAY '72' [20] to R 0.071. Both structures were refined using a weighting scheme of the type $\sqrt{w} = 1$ for $F_o < F^*$ and $\sqrt{w} = F^*/F$ for $F > F^*$.

TABLE 2

Atomic co-ordinates ($\times 10^4$ for) (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	2 547(7)	859(3)	1 261(1)
S(2)	2 363(16)	2 564(5)	1 669(3)
S(16)	3 240(11)	34(6)	2 106(3)
C(3)	4 527(48)	3 414(27)	1 540(14)
C(4)	6 467(50)	2 708(25)	1 526(12)
C(5)	7 133(67)	2 297(29)	943(13)
N(6)	5 558(37)	1 490(19)	754(10)
C(7)	5 477(40)	1 168(21)	260(11)
C(8)	4 047(42)	462(20)	67(11)
N(9)	2 471(44)	222(15)	451(7)
C(10)	965(42)	−413(20)	323(10)
C(11)	−422(44)	−600(22)	712(12)
N(12)	−307(32)	−72(18)	1 171(9)
C(13)	−1 683(39)	−275(21)	1 629(9)
C(14)	−1 012(46)	153(25)	2 202(12)
C(15)	935(45)	−407(24)	2 387(12)
C(17)	3 817(51)	1 211(25)	2 536(13)
C(18)	2 679(60)	2 153(21)	2 405(11)
C(20)	7 272(68)	1 508(27)	−104(12)
C(21)	3 876(48)	28(24)	−451(11)
C(22)	2 365(57)	−595(21)	−599(11)
C(23)	892(42)	−826(23)	−199(10)
C(24)	−2 111(51)	−1 419(21)	619(11)
Cl	−2 747(17)	−1 839(7)	−1 368(4)
O(1)	−2 958(57)	−2 199(25)	−831(15)
O(2)	−4 629(52)	−1 981(33)	−1 565(12)
O(3)	−1 750(95)	−2 413(27)	−1 696(23)
O(4)	−2 095(48)	−770(20)	−1 361(8)

TABLE 3

Atomic co-ordinates ($\times 10^4$) for (2) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ag	2 299(1)	2 542(0)	2 155(1)
S(2)	744(3)	3 190(2)	1 514(3)
C(3)	1 392(16)	3 773(7)	1 129(17)
C(4)	2 176(21)	4 023(7)	2 047(22)
C(5)	3 312(12)	3 869(6)	2 471(14)
N(6)	3 473(9)	3 339(4)	2 960(10)
C(7)	4 402(11)	3 220(5)	3 622(11)
C(8)	4 500(9)	2 681(5)	4 193(10)
N(9)	3 800(7)	2 305(4)	3 656(9)
C(10)	3 843(10)	1 805(5)	4 133(11)
C(11)	3 031(10)	1 410(5)	3 503(11)
N(12)	2 216(9)	1 612(4)	2 774(10)
C(13)	1 336(11)	1 238(6)	2 131(13)
C(14)	525(12)	1 498(6)	1 107(17)
C(15)	834(13)	1 616(7)	−15(15)
S(16)	1 692(3)	2 185(2)	−51(3)
C(17)	757(11)	2 696(6)	−698(11)
C(18)	105(11)	2 935(7)	28(13)
C(20)	5 355(10)	3 597(5)	3 946(14)
C(21)	5 318(10)	2 559(6)	5 244(11)
C(22)	5 364(11)	2 053(7)	5 723(13)
C(23)	4 644(11)	1 675(6)	5 170(12)
C(24)	3 244(13)	824(5)	3 798(14)
B	7 138(10)	985(5)	3 170(13)
C(31)	7 988(10)	609(5)	2 685(12)
C(32)	7 827(11)	503(6)	1 446(12)
C(33)	8 572(13)	230(6)	981(14)
C(34)	9 510(12)	46(6)	1 815(17)
C(35)	9 712(11)	137(6)	3 020(16)
C(36)	8 939(10)	407(5)	3 415(11)
C(41)	7 458(9)	1 596(5)	3 082(11)
C(42)	7 229(10)	1 993(5)	3 841(11)
C(43)	7 466(11)	2 533(5)	3 707(13)
C(44)	7 919(11)	2 702(6)	2 855(15)
C(45)	8 135(10)	2 337(7)	2 083(13)
C(46)	7 917(10)	1 794(6)	2 197(11)
C(51)	7 188(10)	821(5)	4 591(11)
C(52)	8 055(10)	982(5)	5 558(13)
C(53)	8 065(13)	879(6)	6 759(13)
C(54)	7 219(16)	638(6)	7 050(15)
C(55)	6 386(12)	477(5)	6 101(15)
C(56)	6 353(10)	567(5)	4 909(13)
C(61)	5 915(9)	891(5)	2 310(10)
C(62)	5 562(11)	378(5)	1 841(12)
C(63)	4 492(12)	310(6)	1 149(12)
C(64)	3 817(10)	725(6)	870(11)
C(65)	4 138(11)	1 232(6)	1 333(12)
C(66)	5 177(9)	1 295(5)	2 011(11)

Values of F^* of 30 in (1) and 100 in (2) gave similar values of $w\Delta^2$ over ranges of F_o and $(\sin\theta)/\lambda$. Both structures were refined at the University of London Computer Centre. Scattering factors and dispersion corrections were taken from International Tables.[21] Non-hydrogen-atom co-ordinates for (1) and (2) are given in Tables 2 and 3, bond lengths and angles in Table 4, torsion angles in Table 5, and least-squares planes in Table 6. Hydrogen-atom parameters, anisotropic and isotropic thermal parameters, and structure factors are given in Supplementary Publication No. SUP 22798 (24 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 4

Molecular dimensions, distances (Å), and angles (°) in (1) and (2)

(*a*) Cation

	(1), M = Cu	(2), M = Ag
M–S(2)	2.328(7)	2.555(4)
M–S(16)	2.324(8)	2.600(4)
M–N(6)	2.519(25)	2.537(10)
M–N(9)	2.103(17)	2.317(9)
M–N(12)	2.279(22)	2.441(10)
S(2)–M–S(16)	92.2(3)	85.8(1)
S(2)–M–N(6)	88.2(6)	88.0(3)
S(2)–M–N(9)	136.8(5)	146.1(3)
S(2)–M–N(12)	116.8(6)	126.4(3)
S(16)–M–N(6)	113.1(6)	128.3(3)
S(16)–M–N(9)	130.7(6)	127.7(3)
S(16)–M–N(12)	92.1(6)	86.0(3)
N(6)–M–N(9)	71.8(9)	67.6(3)
N(6)–M–N(12)	144.3(8)	135.5(3)
N(9)–M–N(12)	72.6(9)	68.7(3)
C(3)–S(2)	1.84(3)	1.80(2)
S(2)–C(18)	1.86(3)	1.80(1)
S(16–C(15)	1.80(3)	1.82(2)
S(16)–C(17)	1.83(3)	1.79(1)
C(3)–C(4)	1.59(5)	1.40(3)
C(4)–C(5)	1.56(4)	1.49(3)
C(5)–N(6)	1.54(5)	1.43(2)
N(6)–C(7)	1.26(4)	1.29(2)
C(7)–C(8)	1.39(4)	1.49(2)
C(7)–C(20)	1.57(5)	1.53(2)
C(8)–N(9)	1.45(4)	1.34(1)
C(8)–C(21)	1.36(4)	1.42(1)
N(9)–C(10)	1.33(4)	1.36(2)
C(10)–C(11)	1.35(4)	1.49(2)
C(10)–C(23)	1.36(4)	1.40(2)
C(11)–N(12)	1.29(3)	1.27(2)
C(11)–C(24)	1.58(4)	1.51(2)
N(12)–C(13)	1.47(3)	1.52(2)
C(13)–C(14)	1.55(4)	1.50(2)
C(14)–C(15)	1.57(4)	1.48(3)
C(17)–C(18)	1.44(4)	1.47(2)
C(21)–C(22)	1.37(2)	1.37(2)
C(22)–C(23)	1.37(2)	1.37(2)
M–S(2)–C(3)	113.7(11)	101.0(6)
M–S(2)–C(18)	98.5(9)	100.3(5)
C(3)–S(2)–C(18)	102.9(16)	100.7(8)
S(2)–C(3)–C(4)	111(2)	118.4(15)
C(3)–C(4)–C(5)	116(3)	126.6(19)
C(4)–C(5)–N(6)	106(3)	113.3(14)
C(5)–N(6)–M	129(2)	125.0(8)
C(5)–N(6)–C(7)	121(2)	114.8(8)
M–N(6)–C(7)	109(2)	117.5(11)
N(6)–C(7)–C(8)	123(2)	115.1(12)
N(6)–C(7)–C(20)	114(2)	125.7(12)
C(8)–C(7)–C(20)	122(2)	118.9(10)
C(7)–C(8)–N(9)	116(2)	117.7(10)
C(7)–C(8)–C(21)	128(2)	121.7(11)
N(9)–C(8)–C(21)	116(2)	120.6(12)
C(8)–N(9)–M	120(2)	120.2(8)
C(8)–N(9)–C(10)	123(2)	120.7(9)
M–N(9)–C(10)	117(2)	117.9(11)
N(9)–C(10)–C(11)	119(2)	117.8(9)
N(9)–C(10)–C(23)	118(2)	119.7(11)
C(11)–C(10)–C(23)	123(3)	122.4(12)
C(10)–C(11)–C(12)	118(3)	114.9(11)
C(10)–C(11)–C(24)	123(2)	117.9(10)
N(12)–C(11)–C(24)	120(2)	127.2(11)
C(11)–N(12)–C(13)	121(2)	118.1(10)
C(11)–N(12)–M	113(2)	118.3(8)
C(13)–N(12)–M	124(2)	122.3(7)
N(12)–C(13)–C(14)	115(2)	113.6(10)
C(13)–C(14)–C(15)	111(2)	117.6(11)
C(14)–C(15)–S(16)	120(2)	119.5(8)
C(15)–S(16)–M	106.4(10)	105.9(7)
C(17)–S(16)–M	101.0(10)	98.9(7)
C(15)–S(16)–C(17)	102.6(15)	101.9(12)
S(16)–C(17)–C(18)	113.8(21)	119.2(12)
C(17)–C(18)–S(2)	119.6(21)	121.3(11)

TABLE 4 (*Continued*)

(*b*) Anions

(*i*) $[\mathrm{ClO_4}]^-$ in (1)

Cl–O(1)	1.37(4)	O(1)–Cl–O(2)	100(2)
Cl–O(2)	1.38(4)	O(1)–Cl–O(3)	118(3)
Cl–O(3)	1.26(5)	O(1)–Cl–O(4)	109(2)
Cl–O(4)	1.39(3)	O(2)–Cl–O(3)	103(3)
		O(2)–Cl–O(4)	115(2)
		O(3)–Cl–O(4)	112(3)

(*ii*) $[\mathrm{BPh_4}]^-$ in (2)

	$n = 3$	$n = 4$	$n = 5$	$n = 6$
B–C(*n*1)	1.57(2)	1.59(2)	1.57(2)	1.57(2)
C(*n*1)–C(*n*2)	1.40(2)	1.40(2)	1.42(2)	1.42(2)
C(*n*2)–C(*n*3)	1.40(2)	1.41(2)	1.40(2)	1.43(2)
C(*n*3)–C(*n*4)	1.42(2)	1.40(2)	1.38(3)	1.35(2)
C(*n*4)–C(*n*5)	1.36(2)	1.34(2)	1.38(2)	1.39(2)
C(*n*5)–C(*n*6)	1.39(2)	1.40(2)	1.38(2)	1.38(2)
C(*n*6)–C(*n*1)	1.40(2)	1.41(2)	1.40(2)	1.38(2)
B–C(*n*1)–C(*n*2)	120.8(10)	122.3(12)	120.2(11)	121.2(11)
B–C(*n*1)–C(*n*6)	125.1(12)	123.7(12)	122.8(10)	123.2(11)
C(*n*2)–C(*n*1)–C(*n*6)	113.9(13)	113.9(16)	116.8(12)	115.6(10)
C(*n*1)–C(*n*2)–C(*n*3)	122.9(12)	121.4(13)	120.0(13)	119.3(12)
C(*n*2)–C(*n*3)–C(*n*4)	117.8(14)	122.4(14)	122.1(13)	121.9(13)
C(*n*3)–C(*n*4)–C(*n*5)	122.0(16)	118.6(14)	117.1(16)	119.8(12)
C(*n*4)–C(*n*5)–C(*n*6)	117.0(13)	120.5(15)	122.9(16)	117.9(12)
C(*n*5)–C(*n*6)–C(*n*1)	126.3(13)	123.1(13)	121.2(12)	125.2(12)

C(31)–B–C(41)	107.9(11)	C(41)–B–C(51)	110.9(10)
C(31)–B–C(51)	108.7(9)	C(41)–B–C(51)	109.1(9)
C(31)–B–C(61)	110.4(10)	C(51)–B–C(61)	108.9(11)

Angles between phenyl rings: 3–4 78.3, 3–5 57.4, 3–6 59.5, 4–5 63.4, 4–6 81.8, 5–6 84.5.

DISCUSSION

Both structures contain discrete cations and anions. In both cations the metal atoms are bonded to all five donor atoms of the macrocycle as shown in Figures 1 and 2. The geometries of the two co-ordination spheres are similar but by no means the same. Angles subtended at the metal vary by a mean of 6.6° between the two cations, with a maximum deviation of 14.8°. This disparity is probably largely due to the difference in metal-ion radii, the latest values being 0.68 Å for $\mathrm{Cu^I}$ and 1.09 Å for $\mathrm{Ag^I}$ in five-co-ordinate complexes.[22] This difference of 0.41 Å, if representative, is not borne out by the difference between the metal–ligand bond lengths in the two structures under discussion. However, this is a not unexpected situation in complexes of macrocyclic ligands where there must often be a compromise between preferred bond length and macrocycle conformation.

TABLE 5

Torsion angles (°)

	$[\mathrm{CuL^1}]^+$	$[\mathrm{AgL^1}]^+$
N(6)–C(5)–C(4)–C(3)	−66.5	−61.4
C(5)–C(4)–C(3)–S(2)	92.8	84.0
C(4)–C(3)–S(2)–C(18)	70.2	−164.9
C(3)–S(2)–C(18)–C(17)	−86.8	70.9
S(2)–C(18)–C(17)–S(16)	−46.5	50.6
C(18)–C(17)–S(16)–C(15)	−74.8	73.6
C(17)–S(16)–C(15)–C(14)	82.0	−95.6
S(16)–C(15)–C(14)–C(13)	79.3	−76.1
C(15)–C(14)–C(13)–N(12)	−61.5	73.1

In both structures the M–N(9) distances are the shortest by a considerable margin [2.103(17) for M = Cu and 2.317(9) Å for M = Ag]. This is a previously noted [2,11,12] feature of complexes of 2,6-diacetylpyridine although the effect is not usually so marked. In $[AgL^2]^+$ for example, which has a similar five-co-ordinate geometry, the Ag–N(9) distances are 2.365 and 2.393 Å with Ag–N(6), Ag–N(12) 2.555, 2.492, and 2.504, 2.514 Å respectively in the two molecules of the asymmetric unit.[2] The Ag–S distances in $[AgL^1]^+$ are 2.555 and 2.600 Å. There are few five-co-ordinate silver(I) structures available for comparison but in four macrocycle complexes [2-4] the Ag–N distances range from 2.364 to 2.568 Å with a mean of 2.473 Å (21 values) while in two of these complexes [4] the Ag–S distances range from 2.526 to 3.005 Å with a mean of 2.74 Å (10 values). Thus it would appear that there is a fair compatibility in the sizes of the Ag^I ion and of the L^1 macrocycle hole.

The variations in bond lengths in the copper(I) complex (1) are much larger. The two Cu–imino-nitrogen bonds at 2.519(25) and 2.279(22) Å are relatively long, and differ by 0.24 Å, while the two Cu–S bonds are relatively short at 2.328(7) and 2.324(8) Å. Considerably shorter Cu^I–N distances [2.008—2.252 Å with a mean of 2.13 Å (seven values)] are found in two previously reported five-co-ordinate copper(I) complexes.[5,23] There do not appear to be any five-co-ordinate copper(I) structures containing a Cu–S bond. However, in the distorted tetrahedral copper(I) complex [14] of bis[2-(ethylthio)ethyl][2-(2-pyridyl)ethyl]amine the two Cu–S distances are 2.247 and 2.342 Å while in another distorted tetrahedral complex [8] of a 'N_3S' ligand containing thiolate sulphur the Cu–S distance is considerably shorter at 2.19 Å. It appears that the macrocycle L^1 is too large for the Cu^I ion so that the pyridine nitrogen and the two sulphur atoms are tightly bound with the remaining donor atoms fitting in as best they can. Indeed, the Cu–N(6) bond is 0.19 Å longer than the Cu–S bonds. Despite these large variations in bond length the conformation of the macrocycle is more symmetrical in $[CuL^1]^+$ than in $[AgL^1]^+$. In particular, the torsion angles (Table 5) show that $[CuL^1]^+$ has an approximate two-fold axis running through Cu–N(9) with S(2) and S(16) 1.43 and −1.75 Å from the MN_3 plane. In $[AgL^1]^+$, on the other hand, S(2) and S(16) are 0.98 and −1.95 Å from this plane. In addition, in $[AgL^1]^+$ there are considerable variations between comparable torsion angles. Thus one of the C–C–S–C torsion angles is −164.9° while the other three are *ca.* 80°. Despite these distortions, however, the best description of the immediate co-ordination sphere of the $[AgL^1]^+$ complex cation is that with a two-fold axis. Both structures are close to trigonal bipyramids with the two sulphur atoms in equatorial positions; the major deviation from

TABLE 6

Least-squares planes. Distances (Å) of atoms from the planes are given in square brackets for the copper complex and then the silver complex. Atoms not contributing to the plane are marked with an asterisk

Plane 1: M, N(12), S(16)
[C(13) * 0.80, C(14) * 1.63, C(15) * 0.69]
[C(13) * 0.83, C(14) * 1.66, C(15) * 0.95]

Plane 2: M, S(2), S(16)
[C(17) * 0.41, C(18) * −0.14]
[C(17) * 0.34, C(18) * −0.21]

Plane 3: N, S(2), N(6)
[C(3) * 0.27, C(4) * 1.28, C(5) * 0.64]
[C(3) * 0.97, C(4) * 0.46, C(5) * 0.60]

Plane 4: M, N(6), N(9), N(12)
[Cu −0.03, N(6), 0.02, N(9) −0.02, N(12) 0.02, S(2) * 1.43, S(16) * −1.75]
[Ag −0.10, N(6) 0.08, N(9) −0.07, N(12) 0.09, S(2) * 0.98, S(16) * −1.95]

Plane 5: Pyridine ring
[C(8) 0.01, N(9) 0.01, C(10) −0.01, C(21) 0.00, C(22) −0.01, C(23) 0.01, C(7) * −0.06, C(11) * −0.00, N(6) * 0.01, C(5) * −0.11, N(12) * −0.15, C(13) * −0.09, C(20) * −0.04, C(24) * 0.14, Cu * −0.02]
[C(8) 0.01, N(9) −0.01, C(10) 0.01, C(21) 0.01, C(22) 0.00, C(23) −0.00, C(7) * −0.01, C(11) * −0.01, N(6) * 0.45, C(5) * 0.56, N(12) * 0.35, C(13) * 0.43, C(20) * −0.43, C(24) * −0.36, Ag * 0.39]

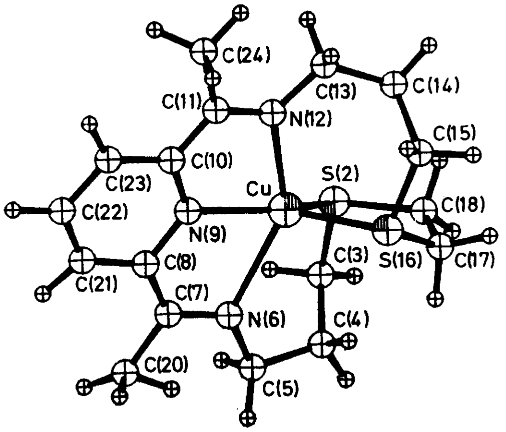

FIGURE 1 The structure of $[CuL^1]^+$

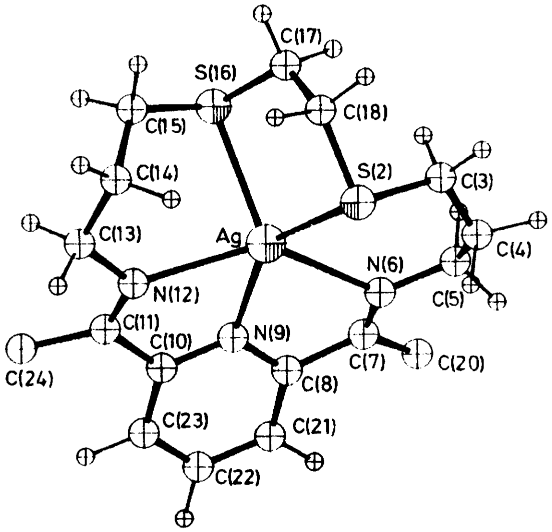

FIGURE 2 The structure of $[AgL^1]^+$

this idealized geometry is a consequence of the N–M–N angles being *ca.* 72°.

A further reflection of the greater distortion in the co-ordination sphere of the silver(I) compared to the copper(I) complex is that in the former C(5), N(6), C(13), and N(12) all lie *ca.* 0.45 Å to one side of the pyridine ring, while in $[CuL^1]^+$ the displacements are smaller at *ca.* 0.1 Å. Also, in $[AgL^1]^+$ the metal ion is 0.39 Å to one side of the pyridine-ring plane as compared to 0.02 Å in the copper(I) complex. These observations reinforce the view that the silver(I) ion is the better fit for the macrocycle cavity and that at the expense of a few adjustments in macrocycle conformation it is possible to place all five donor atoms at acceptable bonding distances. However, for the complex of the smaller copper(I) ion, the adjustments become too great. The macrocycle therefore adopts its preferred C_2 conformation in which the pyridine nitrogen and the two sulphur atoms are strongly bound, the two imino-nitrogens fitting in as best they can. It is noteworthy that the macrocycle does not adopt one of its other (folded) conformations which would permit a more equitable distribution of metal–donor atom distances. Examples are the transition-metal complexes $[FeL^1(NCS)][BPh_4]$ and $[Cu^{II}L^1][ClO_4]_2$ in which the three nitrogens of the trimethine group together with one sulphur atom comprise an approximate square plane with the second sulphur atom occupying one axial position of an octahedron [iron(II) complex] or square pyramid [copper(II) complex].[13]

The conformations of the six-membered rings are all chairs but as can be seen from Table 6, far from regular ones. Thus C(14) is 1.66 Å, but C(4) only 0.46 Å from the Ag, S, N planes in $[AgL^1]^+$ indicating that C(4) is contained in a very flattened chair. In both structures the dimensions of the anions are as expected; even the perchlorate anion is ordered. There are no significant contacts between cations and anions. The shortest distance between non-hydrogen atoms is 3.11 Å in (1) between O(3) and C(17) ($\frac{1}{2} - x, -y, -\frac{1}{2} + z$). There are no Cu $\cdots$ O distances <3.75 Å. In (2) there are no contacts <3.50 Å, a surprisingly high value indicating loose packing as indeed does the very low density.

EXPERIMENTAL

Preparation of the Complexes of L^1.—2,6-Diacetylpyridine was used as supplied. 1,10-Diamino-4,7-dithiadecane was prepared by the method of Dwyer and Lions.[24]

$[AgL^1][ClO_4]$. 2,6-Diacetylpyridine (0.02 mol) in methanol (50 cm^3) was added witth stirring to a solution of $Ag[NO_3]$ (0.02 mol) in methanol (400 cm^3). To this light yellow solution was added a solution of 1,10-diamino-4,7-dithiadecane (0.02 mol) in methanol (50 cm^3). The mixture was heated under reflux for at least 12 h during which time the yellow colour intensified and some silver metal separated. The solution was filtered hot into a methanolic solution of $Na[ClO_4]\cdot H_2O$ (6 g in 50 cm^3) from which yellow crystals of product separated on cooling in 65—70% yield.

$[AgL^1][BPh_4]$. To a hot solution of the perchlorate complex in methanol one equivalent of $Na[BPh_4]$ was added. The yellow product which separated on standing was recrystallised from methanol (yield 74%).

$[Cu^{II}L^1][ClO_4]_2$. A solution of $Cu[ClO_4]_2\cdot 6H_2O$ in methanol (0.02 mol in 20 cm^3) was added to a solution of $[AgL^1][ClO_4]$ (0.02 mol) in methanol (150 cm^3). An almost immediate colour change from yellow to dark blue occurred and a blue powder separated. This was recrystallised from a methanol–acetonitrile solvent mixture to give blue needles of product in 70% yield.

$[Cu^{II}L^1][BPh_4]_2$. To a solution of $[Cu^{II}L^1][ClO_4]_2$ (0.002 mol) in a 1 : 1 methanol–acetonitrile mixture was added $Na[BPh_4]$ (0.004 mol) at room temperature. The blue-green product slowly separated in 75% yield.

$[Cu^{I}L^1][BPh_4]$. A solution of $[Cu^{II}L^1][BPh_4]_2$ (0.002 mol) in methanol or acetonitrile (100 cm^3) was heated to reflux for 30 min, during which time the colour changed from green to dark brown. After concentration the product separated as brown plates in *ca.* 55% yield.

$[Cu^{I}L^1][ClO_4]$. To a hot solution of $[Cu^{II}L^1][ClO_4]_2$ (0.002 mol) in methanol–acetonitrile (100 cm^3), $Na[BPh_4]$ (0.002 mol) in methanol (20 cm^3) was added. The colour changed from green to brown. After filtering hot, the filtrate was concentrated to yield brown plates in 50% yield.

An alternative method for the preparation of the above complex was to use an equimolar amount of solid Na[OMe] in place of $Na[BPh_4]$. A slightly lower yield was obtained.

Preparation of RL^1.—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 Na[OH] in water (5 g in 10 cm^3) was added and the RL^1 so liberated was extracted into chloroform. Rotary evaporation yielded RL^1 as a yellow oil, in 45—55% yield.

Preparation of the Complexes of RL^1.—$[Cu^{II}(RL^1)][ClO_4]_2$. To a hot solution of RL^1 (0.002 mol) in methanol (50 cm^3) was added a solution of $Cu[ClO_4]_2\cdot 6H_2O$ (0.002 mol) in methanol (100 cm^3). The resulting deep blue solution was refluxed for 15 min, filtered hot, and allowed to concentrate slowly. A microcrystalline blue solid separated at low volume. It was washed with cold ethanol. Yield 60%.

$[Cu^{I}(RL^1)][BPh_4]$. To a hot solution of $[Cu^{II}(RL^1)][ClO_4]_2$ (0.001 mol) in acetonitrile (100 cm^3) was added $Na[BPh_4]$ (0.002 mol) in methanol (20 cm^3). The mixture was refluxed under N_2 for 1 h during which time the colour gradually changed from blue to amber. After filtering and rotary evaporation, a small amount (20%) of an orange-brown material, believed from i.r. spectra and chemical analysis to be an impure form of the desired product, was obtained.

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