

The Non-template Synthesis of Dinucleating Macrocyclic Schiff Bases Derived from Thiophen, and their Di-silver Complexes; X-Ray Crystal Structures of two of the Products

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Summary Novel macrocyclic Schiff bases containing thiophen are prepared by the non-template condensation of α,ω -amino-ethers with thiophen-2,5-dicarbaldehyde, and the corresponding di-silver complexes are prepared either by carrying out the reaction in the presence of silver cations, or by adding silver cations to the preformed macrocycle; the X-ray structures of 3,9,16,22-tetra-aza-6,19-dioxa-27,28-dithiatricyclo[22.2.1.1^{11,14}]octacos-2,9,11,13,15,22,24,26-octaene and diaqua-(3,12,19,28-tetra-aza-6,9,22,25-tetraoxa-33,34-dithiatricyclo[28.2.1.1^{14,17}]-tetratriaconta-2,12,14,16,18,28,30,32-octaene)bisperchloratodisilver(I) have been determined.

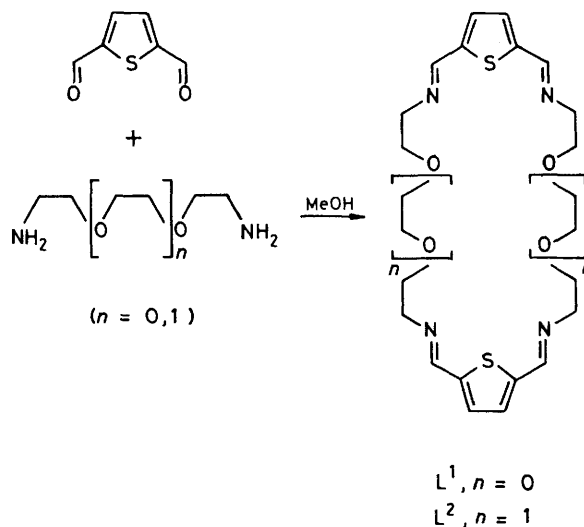
THE design and synthesis of dinucleating ligands and their metal complexes has been the subject of much recent interest.¹⁻³ Several dinuclear complexes of macrocyclic Schiff bases derived from pyridinyl precursors have been reported^{4,5} but the corresponding free macrocyclic tetraimines have not yet been isolated. We have found that the reaction of equimolar amounts of thiophen-2,5-dicarbaldehyde with α,ω -amino-ethers in methanol gives a facile synthesis of free tetraimine macrocycles. When the reaction mixture is refluxed for 2-3 h, the yield of macrocycle is 15-20%, but if the mixture is stirred at room temperature overnight the yield increases to 50-55%.

That cyclisation has occurred in the reaction is indicated in the i.r. (KBr discs) spectra which show no bands ascribable

† ¹H N.m.r. (CDCl₃): L¹, δ 3.63 (m, 16 H, CH₂), 6.91 (s, 4 H, CH-thiophen), and 8.13 (s, 4 H, CH=N); L², δ 3.57 (s, 8 H, CH₂-N), 3.71 (s, 16 H, CH₂-O), 7.23 (s, 4 H, CH-thiophen), and 8.29 (s, 4 H, CH=N).

‡ The '1+1' and '2+2' nomenclature is used as adopted in reference 2.

to free amine or carbonyl groups yet have $\nu(\text{C}=\text{N})$ at 1638 cm^{-1} (L¹) and 1633 cm^{-1} (L²). There are no resonances due to an aldehyde proton in the ¹H n.m.r. spectra of L¹ and L².† It is possible to suggest that a '1 + 1' condensation has occurred rather than the above '2 + 2' condensation,‡ but the mass spectra give M⁺ ions at *m/e* values corre-



sponding to '2 + 2' (L^1 , 416; L^2 , 504). Confirmation of the '2 + 2' structure came from the X-ray crystal structure of L^1 .

The reaction was also carried out in the presence of silver nitrate in methanol; on addition of the reaction mixture to a methanolic solution of sodium perchlorate the di-silver complexes $L^1(AgClO_4)_2$ and $L^2(AgClO_4)_2 \cdot 2H_2O$ were precipitated in good yield. The silver complexes were also prepared from the free macrocycle.[§] Their i.r. spectra (KBr discs) showed a slight lowering of $\nu(C=N)$ to 1630 cm^{-1} (L^1) and 1629 cm^{-1} (L^2) and the mass spectra gave highest peaks corresponding to the free macrocycles.

Crystal data for L^1 : $C_{20}H_{20}N_4O_2S_2$, $M = 416.5$, crystallises from methanol as colourless, irregular bricks; crystal dimensions $0.70 \times 0.62 \times 0.48\text{ mm}$. Orthorhombic, $a = 25.820(13)$, $b = 14.275(6)$, $c = 5.938(2)\text{ \AA}$, $U = 2189(2)\text{ \AA}^3$, $D_m = 1.26$, $Z = 4$, $D_c = 1.269\text{ g cm}^{-3}$, space group $P2_12_12_1$ (from systematic absences), Mo- K_α radiation ($\lambda = 0.71069\text{ \AA}$), $\mu(\text{Mo-}K_\alpha) = 2.53\text{ cm}^{-1}$, $F(000) = 864$.

Three-dimensional X-ray diffraction data were collected in the range $3.5 < 2\theta < 50^\circ$ on a Nicolet Syntex R3 diffractometer by the ω -scan method. 1633 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects; a correction was made for 6.2% intensity loss during data collection based on the monitoring of two reflections. The structure was solved by Patterson, multiple-solution direct-methods, and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions (C-H 0.95 \AA); their contributions were included in structure factor calculations ($B = 8.0\text{ \AA}^2$); limited refinement of positional parameters was permitted. Refinement converged at $R = 0.044$ with allowance for anisotropic thermal motion of all atoms except hydrogen.

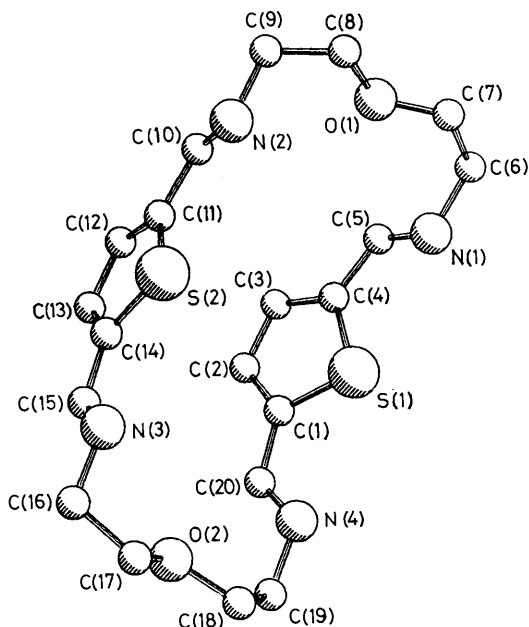


FIGURE 1. Molecular structure of L^1 .

[§] Satisfactory chemical analyses were obtained throughout.

[¶] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Crystal data for $[L^2Ag_2(H_2O)_2]^{2+}(ClO_4^-)_2$: $C_{24}H_{36}Ag_2Cl_2N_4O_{14}S_2$, $M = 955.3$, crystallises from methanol-ethanol as colourless, very fine needles; crystal dimensions $0.51 \times 0.07 \times 0.04\text{ mm}$. Monoclinic, $a = 27.941(16)$, $b = 8.612(6)$, $c = 15.359(9)\text{ \AA}$, $\beta = 102.92(5)^\circ$, $U = 3602(4)\text{ \AA}^3$, $D_m = 1.78$, $Z = 4$, $D_c = 1.762\text{ g cm}^{-3}$, space group $C2/c$ (from systematic absences and confirmed by analysis), Mo- K_α radiation ($\lambda = 0.71069\text{ \AA}$), $\mu(\text{Mo-}K_\alpha) = 14.02\text{ cm}^{-1}$, $F(000) = 1920$.

860 Independent reflections of rather poor quality (collected as for molecule L^1) for which $I/\sigma(I) > 2.0$ were corrected for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least-squares. Hydrogen atoms were placed in calculated positions (C-H 0.95 , O-H 0.90 \AA , $\angle\text{Ag-O-H } 110^\circ$); their contributions were included in structure-factor calculations ($B = 10.0\text{ \AA}^2$) but no refinement of positional parameters was permitted. The two perchlorate ions were disordered about an inversion centre and a 2-fold axis and were refined with constrained T_d symmetry (Cl-O 1.38 \AA). Refinement converged at $R = 0.126$ with an allowance for anisotropic thermal motion of silver and sulphur atoms only. Scattering factors for both structures were taken from ref. 6; unit weights were used throughout the refinements and computer programs used formed part of the Sheffield X-ray system.[¶]

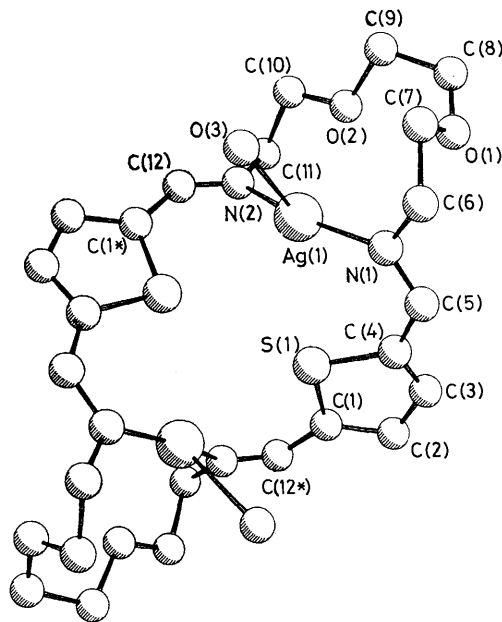


FIGURE 2. Molecular structure of $[L^2Ag_2(H_2O)_2]^{2+}$.

The structures of L^1 and $[L^2Ag_2(H_2O)_2]^{2+}$ are illustrated in Figures 1 and 2 respectively, in each case with the atom labelling used in the corresponding Tables. Mean bond lengths (together with estimated standard deviations) are given in Tables 1 and 2.

TABLE 1. Mean bond lengths^a and estimated standard deviations for L¹.

Bond	Length/Å	Bond	Length/Å
S(1)-C(1)	1.732(6)	N(1)-C(5)	1.255(8)
C(1)-C(2)	1.355(9)	N(1)-C(6)	1.470(9)
C(2)-C(3)	1.416(9)	O(1)-C(7)	1.419(8)
C(4)-C(5)	1.449(8)	C(6)-C(7)	1.491(10)

^a Bond lengths quoted are the mean values of chemically equivalent bonds of the type indicated by the atom labels; individual deviations from the mean values are generally much smaller than the quoted mean estimated standard deviations, individual values of which are almost identical for chemically equivalent bonds.

The molecule L¹ adopts a folded conformation in which two, planar thiophen rings (r.m.s. deviations 0.0024 and 0.0036 Å) lie aligned and approximately parallel although not fully eclipsed, with a mutual inclination of 24.6° and a mean separation of 3.44 Å. The torsion angles about the four saturated carbon-carbon bonds are all ±66.3° (±5.5°). The existence of a silver complex of L¹ suggests

TABLE 2. Mean bond lengths^a and estimated standard deviations for the cation [L²Ag₂(H₂O)₂]²⁺.

Bond	Length/Å	Bond	Length/Å
Ag(1)-N(1)	2.27(4)	S(1)-C(1)	1.79(5)
Ag(1)-N(2)	2.17(4)	C(1)-C(2)	1.37(7)
Ag(1)-O(3)	2.71(7)	C(2)-C(3)	1.42(7)
Ag(1) . . . S(1)	3.100(13)	C(4)-C(5)	1.39(6)
Ag(1) . . . S(1*) ^b	3.187(13)	N(1)-C(5)	1.25(6)
Ag(1) . . . O(2)	2.93(3)	N(1)-C(6)	1.42(7)
O(3)-O(8) ^b	3.04(14)	O(1)-C(7)	1.41(7)
O(3)-O(10) ^b	2.82(14)	C(6)-C(7)	1.54(8)
O(3)-O(4) ^b	3.06(8)	C(8)-C(9)	1.53(8)

^a See footnote to Table 1. ^b Atoms O(8) and O(10) are oxygen atoms of different disorder components of the perchlorate ion situated near the inversion centre ($\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$); atom O(4) is an oxygen atom of one disorder component of the perchlorate ion situated across the two-fold axis (see comment in text). Atom S(1*) is related to atom S(1) by the two-fold symmetry of the cation.

that substantial conformational change will occur on co-ordination.

In [L²Ag₂(H₂O)₂]²⁺ the skeleton of the macrocycle has a twisted-loop conformation with imposed C₂ symmetry; the two symmetry-related silver atoms are each strongly bonded to two nitrogen atoms and, rather remotely, to a water molecule. Other contacts between silver and heteroatoms in the macrocycle are rather too long to be interpreted as covalent bonds; although the distance to one such oxygen [O(2)] is only 0.23 Å greater than that to the water molecule, the remaining oxygen atom is very remote. The co-ordination geometry of each silver atom is very asymmetric, whether the co-ordination number is taken as 3, 4, or 6, and different from that observed in a related di-silver complex of a 28-membered octadentate (all nitrogen donors) macrocycle.⁵ The bis(iminomethyl)thiophen residue is closely planar (r.m.s. deviation 0.024 Å) and the two such symmetry-related residues are mutually inclined at 76.9°. The torsion angles about the saturated carbon-carbon bonds are 58, 47, and -75°. The cation macrocycles are weakly linked together in chains through hydrogen bonds between the co-ordinated water molecules [O(3)] and the disordered perchlorate ions situated at the inversion centres (of Wyckoff type *d*). This perchlorate ion is almost certainly more extensively disordered than so far expressed (based on thermal vibrational parameters and residual electron density) but the limited quantity and rather poor quality of the data do not justify an elaboration of the model. The oxygen-oxygen hydrogen bonded distances (Table 2) are thus typical rather than exact. A further weak hydrogen bond also occurs between O(3) and the disordered perchlorate ion on the 2-fold axis (Wyckoff type *e*).

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