A polymeric tetraimine Schiff base macrocyclic complex of silver(I)

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Abstract

Silver(I)-templated cyclocondensation of pyridine-2,6-dicarbaldehyde and 3-oxa-1,5-diaminopentane yields a dinuclear silver(I) complex of the '2+2' tetraimine Schiff base macrocycle L_1. The crystal structure of the complex recrystallised from acetonitrile shows the product of recrystallisation to be polymeric with cyano-linked dimers being further associated through silver...silver interactions.

Introduction

'2+2' Tetraimine Schiff base macrocycles are readily prepared by the template cyclocondensation of heterocyclic dicarbonyl derivatives and 1,n-diaminoalkanes in 2:2 molar ratio [1, 2]. Disilver(I) complexes have been synthesised of such macrocycles derived from thiophene-2,5-dicarbaldehyde [3, 4] and from 2,6-diacetylpyridine [5–11]. In the latter case the use of functionalised triamines bearing 2-aminoethyl, 2-pyridylmethyl, 2-methoxyethyl and 2-methoxybenzyl substituents led to the synthesis of N,N'-bibracchial macrocyclic complexes of the templating cation in which the macrocycles fold to present molecular clefts into which the metals coordinate [8, 11].

L_1, R = H
L_2, R = CH$_3$
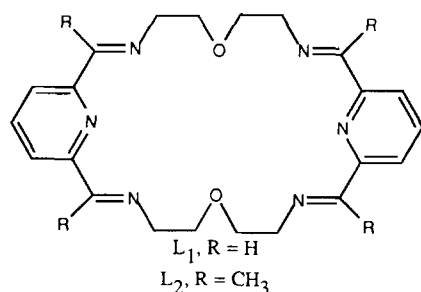
In pursuance of our studies of molecular clefts derived from disilver(I) complexes of tetraimine Schiff base macrocycles we have synthesised (L_1) as its disilver(I) perchlorate complex and herein report also the X-ray crystal structure of the complex recovered after recrystallisation from acetonitrile. The related '2+2' tetraimine Schiff base macrocycle (L_2) has previously been prepared as its mononuclear barium complex by barium-templated cyclocondensation of 2,6-diacetylpyridine and 3-oxa-1,5-diaminopentane, and used in the preparation of dinuclear copper(II) complexes via transmetallation reactions [12].

Experimental

The microanalytical and physicochemical data were recorded as previously described [8].

Synthetic details

A solution of 1,5-diamino-3-oxapentane (5 mmol) in methanol (50 cm^3) was added dropwise over 2 h to a refluxing solution of pyridine-2,6-dicarbaldehyde (5 mmol) and silver nitrate (5 mmol) in methanol (100 cm^3). The solution was then refluxed for a further 5 h after which it was filtered while hot and then allowed to cool prior to being filtered into a methanolic solution of sodium perchlorate (1.5 g in 30 cm^3). An immediate precipitate was obtained which was filtered off and washed with methanol and chloroform. The product was dissolved in acetonitrile (100 cm^3) and warmed on a steam bath. The solution was filtered to give a clear yellow solution which was left to stand undisturbed and in the absence of light for one week at room temperature. A small number of yellow crystals was obtained one of which was suitable for X-ray structural analysis.

Anal. Found: C, 36.8; H, 3.5; N, 12.7. Calc. for $C_{23}H_{26}Ag_2ClN_7O_6$: C, 36.9; H, 3.5; N, 13.1%. IR (KBr disc): ν(CN) 2135, ν(CN(imine)) 1653, ν(pyr) 1583, ν(ClO$_4$) 1090 cm^{-1}. FAB-MS: $P = 647$ amu $[Ag_2(L_1)(CN)]^+$. ^{1}H NMR (CD$_3$CN): 8.26 (s) [4H]; 7.88 (t) [2H]; 7.55 (d) [4H]; 3.85 (dd) [16H].

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TABLE 1. Atomic positional parameters with e.s.d.s in [Ag₂(L₁)(CN)]ClO₄·0.275H₂O

Atom	x	y	z
Ag(1)	−0.11455(10)	0.29942(6)	0.25965(5)
Ag(2)	0 31202(10)	0 45550(8)	0.05897(6)
Cl(1)	0.48173(36)	−0.17850(21)	0.34499(21)
O(1)	−0.0049(7)	0.5932(5)	0.3111(4)
O(2)	0.1409(7)	0 1280(5)	0.0376(4)
O(3)	0.4633(11)	−0.1298(8)	0 4251(6)
O(4)	0.4820(10)	−0 2959(6)	0.3771(8)
O(5)	0.6306(12)	−0 1458(8)	0.2859(8)
O(6)	0 3687(13)	−0 1387(8)	0.2929(8)
O(7)	0.3107(35)	−0.0696(24)	0.0806(22)
N(1)	0.0115(7)	0.2021(6)	0.3791(5)
N(2)	−0.0434(9)	0.0924(6)	0.2452(5)
N(3)	−0.1579(8)	0.3867(6)	0 4086(5)
N(4)	0.3974(9)	0.2678(7)	0 0198(6)
N(5)	0.4139(8)	0 3364(6)	0.1866(5)
N(6)	0.3053(9)	0 5408(6)	0.2037(6)
N(7)	−0.2174(10)	0.4484(7)	0.0607(6)
N(7A)	−0.1706(11)	0.3979(7)	0.1261(6)
C(1)	0.0199(10)	0.2440(7)	0.4578(6)
C(2)	0 1106(12)	0 1937(10)	0.5254(8)
C(3)	0.1932(13)	0.1021(11)	0.5117(10)
C(4)	0.1841(11)	0.0561(8)	0.4350(8)
C(5)	0.0894(10)	0 1089(7)	0 3708(7)
C(6)	0.0648(11)	0 0586(8)	0.2911(7)
C(7)	−0.0641(12)	0.0406(9)	0.1691(8)
C(8)	−0.0227(11)	0 1178(9)	0.0649(7)
C(9)	0.1994(13)	0.2139(9)	−0.0516(6)
C(10)	0.3714(14)	0.2255(10)	−0.0631(7)
C(11)	0.4496(11)	0.2018(9)	0.0873(7)
C(12)	0.4663(10)	0.2347(8)	0 1784(7)
C(13)	0.5305(11)	0.1616(9)	0.2545(8)
C(14)	0.5415(12)	0 1989(11)	0 3357(8)
C(15)	0.4901(12)	0.3023(10)	0.3440(7)
C(16)	0.4247(10)	0.3696(9)	0.2652(6)
C(17)	0.3660(10)	0 4822(9)	0.2710(7)
C(18)	0.2477(13)	0.6497(9)	0.2089(8)
C(19)	0 0762(13)	0.6582(8)	0.2153(7)
C(20)	−0.1662(11)	0.5817(8)	0.3171(8)
C(21)	−0.2309(11)	0.4937(8)	0.4135(8)
C(22)	−0.0708(10)	0.3449(7)	0.4659(6)
C(23)	−0.1706(11)	0.3979(7)	0 1261(6)
C(23A)	−0.2174(10)	0 4484(7)	0.0607(6)

Atoms C(23), N(7) and C(23A), N(7A) each have occupancies of 0.5. Atoms Cl(1), O(3–O(6) comprise the perchlorate anion. Atoms O(7) is a water molecule of crystallisation with occupancy of 0.275.

Crystal data for $C_{23}H_{26}Ag_2ClN_7O_6 \cdot 0.275H_2O$: M_r = 752.65, crystallises from acetonitrile as clear yellow elongated blocks, crystal dimensions 0.65×0.4×0.25 mm, triclinic, a = 8.758(6), b = 12.367(4), c = 13.978(4) Å, α = 74.39(3), β = 76.41(4), γ = 87.26(5)°, U = 1417.1(12) Å³, Z = 2, D_c = 1.76 g cm⁻³, space group $P\bar{1}$ (C_i^1, No. 2), Mo Kα radiation ($\bar{\lambda}$ = 0.71069 Å), μ(Mo Kα) = 15.13 cm⁻¹, $F(000)$ = 749.37.

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50.0°$ on a Nicolet R3 diffractometer by the omega scan method. The 2864 independent reflections (of 4984 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 7 azimuthal scans (minimum and maximum transmission coefficients 0.452 and 0.529). The structure was solved by direct methods and refined by blocked cascade least-squares methods. The bridging cyano ligand (between symmetry related disilver macrocycles) was found to be statistically disordered end to end. A low occupancy water of crystallisation refined to a population of 0.275 with an isotropic U = 0.15; the occupancy was fixed to permit thermal anisotropic refinement of the oxygen in the final stages. Hydrogen atoms were included in calculated positions or along identified hydrogen bonds, and refined in riding mode. Refinement converged at a final R = 0.0696 (R_w = 0.0583, 364 parameters, mean and maximum δ/σ 0.004, 0.024), with allowance for the thermal anisotropy of all non-hydrogen atoms. A weighting scheme $w^{-1} = \sigma^2(F) + 0.00022(F)^2$ was used in the latter stages of refinement. Minimum and maximum final electron density −0.56 and 0.95 e Å⁻³.

Complex scattering factors were taken from ref. 13 and from the program package SHELXTL [14] as implemented on the Data General DG30 computer. Atomic positional parameters are listed in Table 1. See also 'Supplementary material'.

Results and discussion

The cleft-like structure of the mono-cation [Ag₂-(L₁)(CN)]⁺, with atom labelling, is shown in Fig. 1. Figure 2 illustrates the dimerisation and the association, leading to polymerisation, found in the lattice. Bond lengths and angles with estimated standard deviations are listed in Table 2.
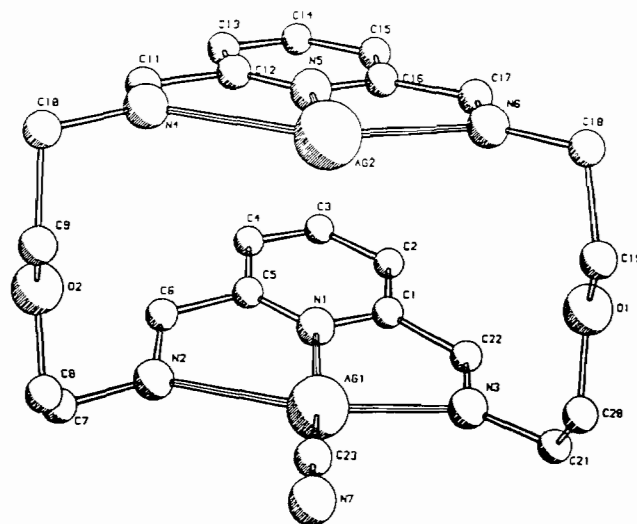

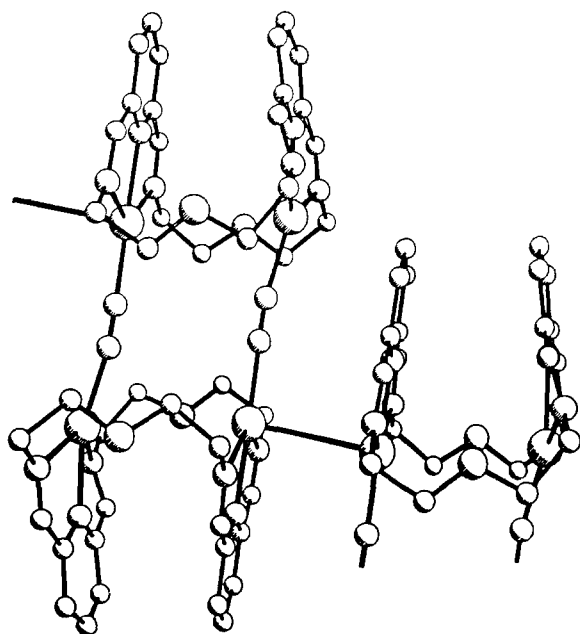Fig. 1. The structure of the mono-cation [Ag₂(L₁)(CN)]⁺

Fig. 2. The dimerisation, and association, leading to polymerisation

The asymmetric unit of the crystal structure comprises two silver(I) ions which are coordinated to the two pyridyl–diimine head units of a fully folded macrocycle, in which the pyridyl fragments lie approximately parallel, and approximately eclipsed (r.m.s. deviations of pyridyl rings 0.012 and 0.005 Å, displacements of silver atoms 0.286 and 0.052 Å, mutual inclination 13.7°, corresponding to a 'bending back' of the pyridyl groups). The formation of such a molecular cleft has been noted in a series of disilver(I) complexes of N,N'-bibracchial tetraimine Schiff base macrocycles [8]. In these complexes the central atoms of the lateral linking chains have been substituent bearing tertiary nitrogen atoms which bond to the silver atoms. There are also bridging imine nitrogen atoms in the complexes with short silver–silver separations — this distance was found to lie in the range 2.91–6.28 Å depending upon the nature of the pendant arm. In the mono-cation $[Ag_2(L_1)(CN)]^+$ the intramolecular silver–silver separation is 4.290 Å and there is no interaction with the oxygen atoms of the two 3-oxapentane chains which link the two approximately parallel and planar units and there are no bridging imino-functions. Also present in the complex are a perchlorate anion, a low occupancy water molecule of crystallisation, and a cyano ligand which coordinates to one silver atom in a site lying *trans* to the pyridyl nitrogen, and which 1,2-bridges to a similar coordination site of the symmetry related second silver atom of an inversion related fragment (through $(-x, 1-y, -z)$): the atoms of the cyano ligand are presumed to be statistically disordered. The origin of the cyano group is uncertain. The IR spectrum of the bulk sample prior

TABLE 2 Bond lengths (Å) and bond angles (°) with e.s.d.s for $[Ag_2(L_1)(CN)]ClO_4$ 0.275H_2O

Bond lengths

Ag(1)–N(1)	2 261(7)	Ag(1)–N(2)	2.655(8)
Ag(1)–N(3)	2 538(8)	Ag(1)–C(23)	2.088(9)
Ag(1)...Ag(2)	4.290		
Ag(2)–N(4)	2.564(9)	Ag(2)–N(5)	2.314(7)
Ag(2)–N(6)	2.509(9)	Ag(2)–N(7)[a]	2.094(9)
Ag(2)–Ag(2)[b]	3.404(2)		
Cl(1)–O(3)	1.383(11)	Cl(1)–O(4)	1.399(8)
Cl(1)–O(5)	1.382(10)	Cl(1)–O(6)	1.360(12)
O(1)–C(19)	1.405(10)	O(1)–C(20)	1.407(12)
O(2)–C(8)	1.396(11)	O(2)–C(9)	1.409(9)
N(1)–C(1)	1.353(13)	N(1)–C(5)	1.330(11)
N(2)–C(6)	1 259(13)	N(2)–C(7)	1.430(15)
N(3)–C(21)	1.453(12)	N(3)–C(22)	1 232(12)
N(4)–C(10)	1.459(16)	N(4)–C(11)	1.233(12)
N(5)–C(12)	1 343(12)	N(5)–C(16)	1.297(13)
N(6)–C(17)	1.234(12)	N(6)–C(18)	1.430(14)
C(1)–C(2)	1.378(14)	C(1)–C(22)	1 464(13)
C(2)–C(3)	1.348(18)	C(3)–C(4)	1.361(20)
C(4)–C(5)	1 379(14)	C(5)–C(6)	1.474(16)
C(7)–C(8)	1.483(13)	C(9)–C(10)	1.487(17)
C(11)–C(12)	1.477(16)	C(12)–C(13)	1.406(14)
C(13)–C(14)	1.359(18)	C(14)–C(15)	1.361(18)
C(15)–C(16)	1 411(14)	C(16)–C(17)	1.477(15)
C(18)–C(19)	1.484(16)	C(20)–C(21)	1.494(12)
N(7)–C(23)	1.113(13)	O(2)...O(7)	2.797
O(2)...H(O7A)	1.80	O(6)...O(7)	3.016
O(6). .H(O7B)	2.02		

Bond angles

N(1)–Ag(1)–N(2)	66.8(3)	N(1)–Ag(1)–N(3)	69.2(2)
N(2)–Ag(1)–N(3)	132.0(2)	C(23)–Ag(1)–N(1)	164.9(3)
C(23)–Ag(1)–N(2)	110.9(3)	C(23)–Ag(1)–N(3)	116.5(3)
N(4)–Ag(2)–N(5)	67.6(3)	N(4)–Ag(2)–N(6)	135.8(2)
N(5)–Ag(2)–N(6)	68 2(3)	N(7)[a]–Ag(2)–N(4)	107.9(3)
N(7)[a]–Ag(2)–N(5)	175.3(3)	N(7)[a]–Ag(2)–N(6)	116.2(3)
Ag(2)[b]–Ag(2)–N(4)	85 8(2)	Ag(2)[b]–Ag(2)–N(5)	87.0(2)
Ag(2)[b]–Ag(2)–N(6)	93.3(2)	Ag(2)[b]–Ag(2)–N(7)[a]	94.1(2)
O(3)–Cl(1)–O(4)	112.6(6)	O(3)–Cl(1)–O(5)	105.0(7)
O(3)–Cl(1)–O(6)	108.4(7)	O(4)–Cl(1)–O(5)	106.1(5)
O(4)–Cl(1)–O(6)	112 7(6)	O(5)–Cl(1)–O(6)	111.8(6)
C(19)–O(1)–C(20)	112.6(8)	C(8)–O(2)–C(9)	114.1(7)
Ag(1)–N(1)–C(1)	119.5(5)	Ag(1)–N(1)–C(5)	122.3(6)
C(1)–N(1)–C(5)	118.0(8)	Ag(1)–N(2)–C(6)	108.0(7)
Ag(1)–N(2)–C(7)	128.6(6)	C(6)–N(2)–C(7)	118.8(9)
Ag(1)–N(3)–C(21)	126 6(6)	Ag(1)–N(3)–C(22)	110.9(6)
C(21)–N(3)–C(22)	119.6(9)	Ag(2)–N(4)–C(10)	128.2(6)
Ag(2)–N(4)–C(11)	113.9(8)	C(10)–N(4)–C(11)	117.3(10)
Ag(2)–N(5)–C(12)	120.6(6)	Ag(2)–N(5)–C(16)	119.6(6)
C(12)–N(5)–C(16)	119.7(8)	Ag(2)–N(6)–C(17)	113.7(7)
Ag(2)–N(6)–C(18)	125.5(7)	C(17)–N(6)–C(18)	120.7(10)
N(1)–C(1)–C(2)	121 1(9)	N(1)–C(1)–C(22)	116.4(8)
C(2)–C(1)–C(22)	122.5(10)	C(1)–C(2)–C(3)	119.1(12)
C(2)–C(3)–C(4)	121.3(12)	C(3)–C(4)–C(5)	117.0(10)
N(1)–C(5)–C(4)	123.4(10)	N(1)–C(5)–C(6)	116.7(8)
C(4)–C(5)–C(6)	119.8(9)	N(2)–C(6)–C(5)	120.6(9)
N(2)–C(7)–C(8)	112 2(9)	O(2)–C(8)–C(7)	106.6(8)
O(2)–C(9)–C(10)	108.1(8)	N(4)–C(10)–C(9)	108.7(8)
N(4)–C(11)–C(12)	120.8(10)	N(5)–C(12)–C(11)	117.0(8)
N(5)–C(12)–C(13)	121.5(10)	C(11)–C(12)–C(13)	121.5(9)
C(12)–C(13)–C(14)	117.5(10)	C(13)–C(14)–C(15)	121.3(10)

(continued)

TABLE 2 (continued)

C(14)–C(15)–C(16)	117.6(11)	N(5)–C(16)–C(15)	122.3(10)
N(5)–C(16)–C(17)	117 9(8)	C(15)–C(16)–C(17)	119 8(10)
N(6)–C(17)–C(16)	120.4(10)	N(6)–C(18)–C(19)	112 2(9)
O(1)–C(19)–C(18)	109.2(8)	O(1)–C(20)–C(21)	106.9(8)
N(3)–C(21)–C(20)	110.0(8)	N(3)–C(22)–C(1)	122.6(9)
Ag(1)–C(23)–N(7)	172 2(8)	Ag(2)^a–N(7)–C(23)	178 1(8)
H(O7A)–O(7)–H(O7B)	116		

Symmetry operations. $^a(-x, 1-y, -z)$; $^b(1-x, 1-y, -z)$

to recrystallisation from acetonitrile shows no band in the region c. 2000–2200 cm^{-1} which could be attributed to ν(CN); after recrystallisation from acetonitrile the spectrum has such a band at 2135 cm^{-1}. The result is unique in that we have not previously detected the presence of the cyano group in a range of disilver(I) macrocyclic complexes which have either been prepared in, or recrystallised from, acetonitrile. We have been able to reproduce the complex by the same route but only in very variable and always very small yields; surprisingly we were not able to synthesise the complex by adding a stoichiometric amount of sodium cyanide to the template reaction. We have observed that as the solvent evaporates from the sample being recrystallised a yellow cyanide-free powder is deposited above the solvent level on the walls of the sample tube. The crystals then grow from the last traces of solvent. At this time we can only conclude that there has been an adventitious formation of the complex during recrystallisation probably due to traces of cyanide impurity in the solvent batch used*.

A further association between these tetra-metallic di-cations occurs between unbridged, symmetry related Ag(2) atoms at a separation of 3.404 Å through a second inversion centre (at $1-x, 1-y, -z$), giving rise to polymerisation parallel to the crystallographic a axis. There is an ongoing debate concerning the origin of such close approaches questioning whether they arise from the formation of a silver–silver bond or whether they are governed by the steric requirements of the ligand [5, 15, 16]. In this complex it is interesting to contrast the inter- and intra-molecular silver–silver separations. There are no intra-molecular bridging atoms and the intra-molecular separation of 4.290 Å is significantly longer than the inter-molecular separation of 3.404 Å. Such a long silver–silver interaction would not normally be viewed as bonding, but its position axial to the AgN$_3$(CN) plane, and the existence [17] of unbridged Ag...Ag interactions at separations of 3.051 and 3.493 Å in {[Ag(imidazole)][ClO$_4$]} lends some credence to this proposal.

*'AnalaR' Grade acetonitrile (minimum assay 99.5%) has <50 ppm CN$^-$ present; the solvent used here is GPR grade (98%)

Further interactions between fragments depend on the intermediacy of the water molecule of crystallisation, which is only present in low occupancy (refined value 27.5%). Where this molecule is present, it forms hydrogen bonded bridges between ether O(2) and perchlorate O(6) (O...O 2.797, 3.016; H...O 1.80, 2.02 Å): its presence does not seem to be structurally critical to the lattice.

Supplementary material

Tables of anisotropic thermal vibrational parameters with e.s.d.s, hydrogen atom position parameters, observed structure amplitudes and calculated structure factors are available from the authors on request.

Acknowledgements

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