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Silver(I)–silver(I) interactions in complexes of pentadentate macrocyclic ligands; crystal and molecular structure of $[Ag_2L_2][BF_4]_2$ (L = 1,11-bis(2′-hydroxyethyl)-4,8;12,16;17,21-trinitrilo-1,2,10,11-tetraazacyclohenicosa-2,4,6,9,12,14,18,20-octaene)

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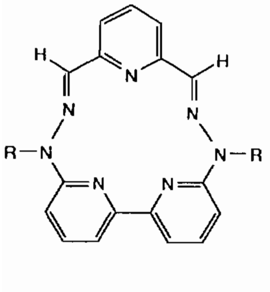
Abstract

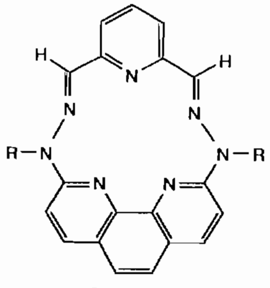
Silver(I) ions do not act as templates for the formation of planar macrocyclic ligands based upon 2,2′-bipyridine or 1,10-phenanthroline, but incorporation of silver(I) into the performed macrocycles, obtained from transient template reactions, is facile. The complexes so obtained have a 1:1 ratio of silver to macrocycle. The crystal structure of the complex $[Ag_2L_2][BF_4]_2$ reveals a dimeric structure in the solid state with two distinct silver environments. Crystallographic data: space group $P2_1/n$, $a = 18.295(3)$, $b = 9.763(2)$, $c = 25.643(5)$ Å, $\beta = 105.03(1)$, $V = 4665$ Å^3, $Z = 4$.

Introduction

Macrocyclic ligands have played a very important role in the development of coordination chemistry during the past 30 years [1, 2]. The majority of ligands which have been studied are tetradentate, commonly possessing an N_4 donor set. We have been interested in the consequences of imposing a planar pentadentate donor set onto a metal ion, and have described the coordination chemistry of a number of open-chain and macrocyclic N_5 donor ligands based upon oligopyridine subunits [3–6]. The majority of the studies of complexes of macrocyclic ligands which we have described have been concerned with first row transition metal ions, and we wish now to describe some novel silver complexes of the planar pentadentate macrocyclic ligands L, L^1 and L^2 containing 2,2′-bipyridine or 1,10-phenanthroline moieties.



L R = CH_2CH_2OH
L^1 R = CH_3



L^2 R = CH_3

Experimental

Infrared spectra were recorded in compressed KBr pellets on Perkin-Elmer FT 910 or Perkin-Elmer 983 spectrophotometers; ^{1}H NMR spectra were recorded on Brüker WM 250 or AM400 spectrometers. Mass spectra were recorded on a Kratos MS50 mass spectrometer. The macrocyclic ligands L, L^1 and L^2 were used as the tetrafluoroborate salts, which were prepared as previously described [4].

Synthesis of $[Ag_2L_2][BF_4]_2$

A solution of $[HL][BF_4]\cdot4H_2O$ (0.112 g, 0.2 mmol) in boiling degassed water (50 ml) was treated with $Ag[BF_4]$ (0.04 g, 0.2 mmol), whereupon an immediate colour change from red to yellow occurred. The mixture was heated to reflux under nitrogen for a further 10 min, concentrated to about 15 ml *in vacuo* and cooled to room temperature, whereupon orange–yellow crystals of $[Ag_2L_2][BF_4]_2$ separated. *Anal.* Found: C, 42.2; H, 3.52; N, 16.2 Calc. for $Ag_2B_2C_{42}F_8H_{42}N_{14}O_4$: C, 42.2; H, 3.5; N, 16.4%. EI MS *m/z* 510.

The analogous complexes $[Ag_2L^1{}_2][BF_4]_2$ (Found: C, 42.5; H, 3.2; N, 18.1 Calc. for $Ag_2B_2C_{38}F_8H_{34}N_{14}$: C, 42.4; H, 3.2; N, 18.2%) and $[Ag_2L^2{}_2][BF_4]_2$ (Found:

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C, 44.7; H, 3.0; N, 17.2 Calc. for $Ag_2B_2C_{42}F_8H_{34}N_{14}$: C, 44.9; H, 3.0; N, 17.4%) were prepared in a precisely similar manner.

X-ray crystallography

A yellow rectangular crystal of $[Ag_2L_2][BF_4]_2 \cdot 3H_2O$ obtained by slow evaporation of an aqueous solution of the complex was mounted on a glass fibre and used for the structure determination. All geometric and intensity data were taken from this crystal using an automated four-circle diffractometer (Syntex $P2_1$) following procedures described previously [4]. Pertinent crystallographic data are given in Table 1. Lattice dimensions were verified by preliminary Weissenberg photography. Intensity data, gathered by the ω–2θ technique, were reduced by routine procedures. Calculations were carried out using the program SHELX [7] on the University of Cambridge IBM 370/165 computer. Empirical absorption corrections were applied.

The two silver atoms of the dimer were located from a Patterson synthesis, and all the remaining non-hydrogen atoms located from subsequent Fourier difference syntheses. The two tetrafluoroborate anions were disordered and were treated as two interlocking tetrahedra of fluorine atoms surrounding the central boron atom. The Ag, N and hydroxyl O atoms were refined anisotropically. Hydrogen atoms were placed in idealised positions on the relevant

TABLE 1. Crystal data for $[Ag_2L_2][BF_4]_2 \cdot 3H_2O$

Formula	$Ag_2B_2C_{42}F_8H_{48}N_{14}O_7$
Formula weight	1250.25
Space group	$P2_{1/n}$
a (Å)	19.295(3)
b (Å)	9.763(2)
c (Å)	25.643(5)
β (°)	105.03(1)
V (Å^3)	4665
Z	4
F(000)	2516
D_{calc} (g/cm^3)	1.78
Crystal size (mm)	0.57×0.42×0.32
μ(Mo Kα) cm^{-1}	8.92
Data collection instrument	Syntex $P2_1$
Radiation	Mo Kα (λ = 0.7107 Å)
Orientation reflections: no.; range (2θ)	15, $15° \leq 2\theta \leq 25°$
Data collection range	$3.0° \leq 2\theta \leq 50.0°$
Temperature (°C)	20
No. of unique data	5075
Total with $F \geq 3\sigma(F)$	4002
R^a	0.058
R'^b	0.062
Weighting scheme	$w = 1.3494/[\sigma^2 F + 0.001 F^2]$
Largest peak (e/Å^3)	0.96

$^a R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. $^b R' = \Sigma w^{1/2}[|F_o| - |F_c|]/\Sigma w^{1/2}|F_o|$.

TABLE 2. Positional parameters (×10^4) and their e.s.d.s. for the binuclear cation in $[Ag_2L_2][BF_4]_2 \cdot 3H_2O$

	x	y	z
Ag(1)	−1316	−220(1)	1583
Ag(2)	−292	1252(1)	800
N(1)	−2130(4)	650(8)	2058(3)
N(2)	−2602(4)	−758(8)	1159(3)
N(3)	−2733(4)	−1637(9)	739(3)
N(4)	−1566(4)	−2374(8)	1132(3)
N(5)	−466(4)	−1896(8)	1986(3)
N(6)	−158(5)	−608(9)	2774(3)
N(7)	−814(4)	−52(9)	2590(3)
N(8)	−397(4)	−885(8)	395(3)
N(9)	663(4)	−337(8)	1253(3)
N(10)	1089(4)	106(9)	1725(3)
N(11)	134(4)	1598(9)	1722(3)
N(12)	−1201(4)	2164(8)	1174(3)
N(13)	−2041(4)	1541(9)	386(3)
N(14)	−1532(4)	685(8)	317(3)
C(1)	−1865(5)	1167(10)	2560(4)
C(2)	−2302(6)	1936(11)	2807(4)
C(3)	−3005(6)	2144(12)	2529(4)
C(4)	−3287(6)	1542(11)	2018(4)
C(5)	−2818(5)	797(10)	1795(4)
C(6)	−3066(6)	17(10)	1288(4)
C(7)	−3472(6)	−1873(12)	404(4)
C(8)	−3902(7)	−2771(13)	702(5)
O(1)	−3574(4)	−3984(9)	885(3)
C(9)	−2154(5)	−2532(10)	726(4)
C(10)	−2187(6)	−3486(10)	320(4)
C(11)	−1578(6)	−4275(11)	358(4)
C(12)	−976(6)	−4161(11)	784(4)
C(13)	−989(5)	−3167(10)	1176(4)
C(14)	−395(5)	−2930(10)	1661(4)
C(15)	219(6)	−3776(12)	1809(4)
C(16)	727(7)	−3502(13)	2300(5)
C(17)	619(6)	−2466(12)	2624(4)
C(18)	−7(6)	−1675(11)	2450(4)
C(19)	296(6)	−269(12)	3312(4)
C(20)	109(8)	−1183(15)	3754(5)
O(2)	659(7)	−997(15)	4226(4)
C(21)	−1127(6)	804(11)	2834(4)
C(22)	−958(5)	−1119(10)	−24(4)
C(23)	−942(6)	−2137(11)	−403(4)
C(24)	−330(5)	−2935(11)	−318(4)
C(25)	239(6)	−2704(11)	111(4)
C(26)	208(6)	−1662(11)	479(4)
C(27)	780(6)	−1348(11)	957(4)
C(28)	1770(6)	−584(12)	1988(4)
C(29)	2414(6)	151(13)	1874(5)
O(3)	2392(4)	184(10)	1322(3)
C(30)	790(6)	1159(11)	1984(4)
C(31)	1169(6)	1694(12)	2486(4)
C(32)	811(6)	2677(13)	2703(5)
C(33)	112(6)	3108(11)	2447(4)
C(34)	−207(5)	2537(10)	1954(4)
C(35)	−949(5)	2868(10)	1641(4)
C(36)	−1402(6)	3819(11)	1803(4)
C(37)	−2073(6)	3986(12)	1468(4)
C(38)	−2334(6)	3295(11)	986(4)
C(39)	−1854(5)	2350(10)	860(4)
C(40)	−2769(5)	1532(11)	25(4)
C(41)	−2880(6)	2635(12)	−413(4)
O(4)	−2433(5)	2318(9)	−760(3)
C(42)	−1605(5)	−252(10)	−51(4)

TABLE 3. Bond distances (Å) and bond angles (°) within the coordination sphere for $[Ag_2L_2][BF_4]_2 \cdot 3H_2O$

Distances (Å)	
Ag(1)–N(1)	2.379(9)
Ag(1)–N(5)	2.357(7)
Ag(1)–N(2)	2.492(8)
Ag(1)–N(4)	2.388(8)
Ag(1)–N(7)	2.516(7)
Ag(1)–Ag(2)	3.472(1)
Ag(1)–N(12)	2.585(8)
Ag(2)–N(8)	2.316(8)
Ag(2)–N(9)	2.458(8)
Ag(2)–N(11)	2.318(7)
Ag(2)–N(12)	2.379(9)
Ag(2)–N(14)	2.455(8)
Angles (°)	
N(1)–Ag(1)–N(2)	65.4(3)
N(1)–Ag(1)–N(4)	119.0(3)
N(1)–Ag(1)–N(5)	120.0(3)
N(1)–Ag(1)–N(7)	65.3(3)
N(1)–Ag(1)–N(12)	91.4(3)
N(2)–Ag(1)–N(4)	63.2(3)
N(2)–Ag(1)–N(5)	123.1(3)
N(2)–Ag(1)–N(7)	122.4(3)
N(2)–Ag(1)–N(12)	101.1(2)
N(4)–Ag(1)–N(5)	68.4(2)
N(4)–Ag(1)–N(7)	122.0(3)
N(4)–Ag(1)–N(12)	128.6(3)
N(5)–Ag(1)–N(7)	63.7(3)
N(5)–Ag(1)–N(12)	132.8(3)
N(7)–Ag(1)–N(12)	107.9(3)
N(8)–Ag(2)–N(9)	67.1(3)
N(8)–Ag(2)–N(11)	123.7(3)
N(8)–Ag(2)–N(12)	122.0(3)
N(8)–Ag(2)–N(14)	67.1(3)
N(9)–Ag(2)–N(11)	65.5(3)
N(9)–Ag(2)–N(12)	125.9(3)
N(9)–Ag(2)–N(14)	127.5(3)
N(11)–Ag(2)–N(12)	68.8(3)
N(11)–Ag(2)–N(14)	126.1(3)
N(12)–Ag(2)–N(14)	64.2(3)

carbon atoms with a fixed isotropic thermal factor for each type. Positional parameters are given in Table 2 and bond distances and angles in the coordination sphere are given in Table 3.

Results and discussion

The coordination chemistry of silver(I) is characterised by the wide variety of coordination numbers and geometries which are exhibited [8]. This is a consequence of the d^{10} configuration, which has no crystal field preference for any particular geometry. The silver(I) ion has an ionic radius of 1.2–1.3 Å, although this value is very dependent upon the coordination number and geometry. The coordination chemistry of silver(I) with macrocyclic ligands is not particularly well developed, and those compounds which have been structurally characterised show a disturbing range of coordination numbers and geometries. In particular, there appears to be little to rationalise the observations that some macrocyclic complexes of silver(I) are mononuclear [9] whilst others are binuclear [10].

Attempts to prepare silver(I) complexes with the planar pentadentate macrocyclic ligands L, L^1 or L^2 by template condensation of the appropriate bishydrazino precursors with 2,6-pyridinedialdehyde or 2,6-diacetylpyridine in the presence of silver(I) salts were unsuccessful. However, the free macrocyclic ligands L, L^1 or L^2 are readily prepared as their salt $[H_2L]^{2+}$, $[H_2L^1]^{2+}$ or $[H_2L^2]^{2+}$ by transient template methods [4], and these react readily with silver(I) salts. The addition of silver(I) salts to red aqueous solutions of $[H_2L]^{2+}$, $[H_2L^1]^{2+}$ or $[H_2L^2]^{2+}$ results in a rapid colour change and the formation of a pale yellow solution. Concentration of these aqueous solutions resulted in the deposition of yellow microcrystalline solids which gave microanalyses consistent with the formulations $[AgL][BF_4]$, $[AgL^1][BF_4]$ or $[AgL^2][BF_4]$, respectively. Recrystallisation of $[AgL][BF_4]$ from water by slow evaporation of the solvent resulted in the formation of X-ray quality crystals of the hydrated complex $\{[AgL][BF_4] \cdot 1.5H_2O\}_n$. The mass spectra of the complexes exhibited highest mass peaks which could be assigned to the species [AgL], $[AgL^1]$ or $[AgL^2]$. In aqueous solution the complexes behaved as 1:1 electrolytes. The above data is all consistent with the formation of simple 1:1 complexes of these pentadentate ligands with silver(I). This is in accord with the formation of a mononuclear 1:1 complex with the related open-chain ligand 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine [11]. However, in the complex with 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine all of the Ag–N bonds are within the range 2.439–2.479 Å, which is in the region expected for the sum of the covalent radius of nitrogen (1.4 Å) and the ionic radius of silver(I) (1.09 Å). The pentadentate macrocyclic ligands L, L^1 or L^2 all have a bonding cavity of radius 2.1 Å which is expected to be too small for a metal ion of radius 1.09 Å. Accordingly, we might expect the silver(I) ion to be displaced from the centre of the plane defined by the five nitrogen donor atoms. In order to further investigate the nature of these silver(I) complexes, we have determined the crystal and molecular structure of the complex $\{[AgL][BF_4] \cdot 1.5H_2O\}_n$.

The X-ray structural analysis of this complex revealed that the cation possessed a dimeric structure, and the correct formulation was $[Ag_2L_2][BF_4]_2 \cdot 3H_2O$. The crystal and molecular structure of the cation in the complex $[Ag_2L_2][BF_4]_2 \cdot 3H_2O$ is shown in Fig. 1. The two silver atoms and the two macrocyclic ligands are non-equivalent. Each silver is coordinated to the five nitrogen donor atoms of the macrocyclic ligand which is associated with it. The Ag–N bonds between the silver atoms and the nitrogen donor atoms of the associated macrocyclic ligands are all within the range 2.316–2.516 Å. These distances fall into two different classes, depending upon the type of the donor atom. The bonds to the nitrogen atoms of the heterocyclic rings are significantly shorter (2.316–2.388 Å) than those to the imine nitrogens (2.455–2.516 Å). This pattern is also seen in the structures of other metal complexes with ligands of this type [3, 4]. The two N_5 donor sets are to all intents and purposes planar, with a greatest deviation of any nitrogen atom from the least-squares plane being 0.035 Å. Furthermore, the two N_5 donor sets are coplanar. The two silver atoms are not in the N_5 planes of the associated ligands, but lie above the donor sets by 0.97 Å (for Ag(1)) and 0.86 Å (for Ag(2)).

The two macrocyclic ligands are not planar, but are distorted into the shape of a shallow dome. This is achieved by tilting of the constituent groups with respect to the N_5 donor plane. Thus, within each macrocyclic ligand the 2,2′-bipyridine and pyridine groups are each essentially planar (greatest deviation from the least-squares N_5 planes 0.12 Å) but are tilted with respect to the N_5 donor plane. For the macrocyclic ligand associated with Ag(1) the 2,2′-bipyridine and pyridine adopt angles of 4.4 and 12.6° with respect to this plane, whereas for the macrocyclic ligand associated with Ag(2) angles of 3.0 and 3.2° are observed. In each case the tilting of the heterocyclic rings is such that the doming of the ligand is away from the silver atom associated with that ligand. The arrangement of the two silver atoms and the two N_5 donor sets is illustrated in Fig. 2. The hydroxyethyl substituents on the non-coordinated nitrogen atoms of the macrocyclic ligands are folded to one the opposite face of the macrocyclic ligand to that occupied by the silver atom. For each macrocyclic ligand, the two hydroxyethyl substituents are both displaced towards the *same* side, as is observed in other complexes, but not in the free ligand [3, 4].

The two {AgL} units are assembled to form a discrete dimeric $[Ag_2L_2]^{2+}$ cation. The two macrocyclic ligands within the dimer are coplanar, and the two silver atoms are both displaced along the *same* vector; the consequence is that Ag(1) occupies a 'sandwich' position between the two macrocyclic ligands, whereas Ag(2) lies above the second macrocyclic ligand and presents a naked metal site. The principal interaction between the two {AgL} subunits is between Ag(1) and N(12) of the second macrocyclic ring, which show a short contact of 2.585 Å.

We attribute the formation of the dimeric structure to the mismatch between the size of the silver ion and the macrocyclic cavity. The expected result is a complex in which the silver ion lies above the pentadentate donor set of the macrocyclic ligand. This is essentially the structure of each of the two individual {AgL} units. The hydroxyethyl substituents are both oriented towards the same side of the macrocyclic ligand, and the silver could be displaced from the N_5 donor plane in the same or the opposite direction to the substituents. The dimer is formed

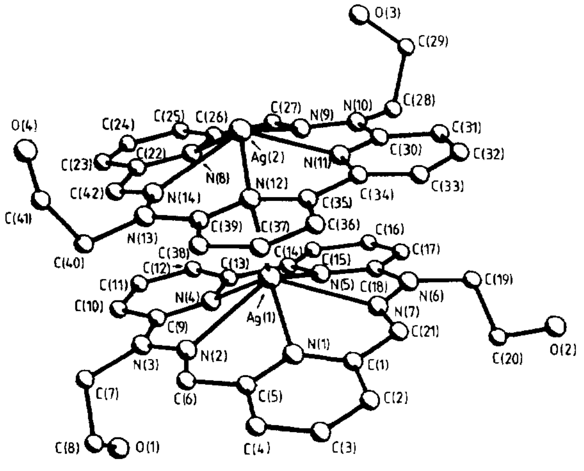

Fig. 1. The crystal and molecular structure of the cation $[Ag_2L_2]^{2+}$ showing the numbering scheme adopted.

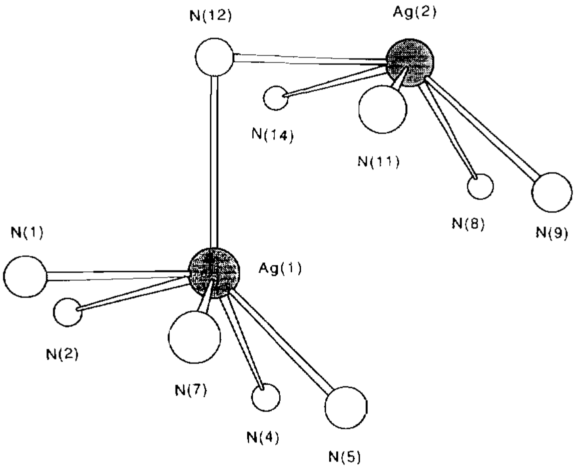

Fig. 2. Schematic representation of the arrangement of the two silver atoms and the nitrogen donor atoms within the complex cation $[Ag_2L_2]^{2+}$.

from one subunit of each structural type. In the case of the silver being displaced towards the hydroxyethyl groups (Ag(2)) the 'exposed' coordination sites of the silver are protected by the substituents, whereas Ag(1) is 'naked'. The structural consequence is the interaction of Ag(1) with the nitrogen of the other subunit. This explanation suggests that the dimeric structure may not necessarily occur with other substituents. We have no direct structural evidence concerning these other silver compounds.

Supplementary material

Tables of full positional parameters, anisotropic and isotropic displacement parameters, hydrogen atom coordinates, details of least-squares planes and complete tables of bond length and bond angles are obtainable from the authors on request.

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