Octa-coordinated environment for Ag^+ involving an N_2O_6 donor set of two sandwiched pyridino crowns. X-ray crystal structure of the complex between tribenzopyridino-15-crown-5 and silver nitrate (2:1)

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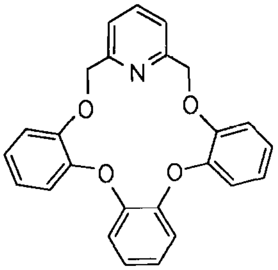
Abstract

The single crystal X-ray analysis of the 2:1 complex between tribenzopyridino-15-crown-5 (**1**) and $AgNO_3$ is reported. Crystals of the complex are triclinic, $P\bar{1}$, with $a=13.182(1)$, $b=13.612(2)$, $c=12.720(1)$ Å, $\alpha=105.39(1)$, $\beta=99.96(1)$, $\gamma=103.04(1)°$ and $D_c=1.54$ g cm^{-3} for $Z=2$. The Ag^+ cation forms a charge separated sandwich structure where Ag^+ is in an octa-coordinated environment involving two nitrogen and six oxygen atoms of the macrorings. The complex has a complete hydrophobic shell.

Introduction

Organic ligands which are highly effective in the complexation of silver are of considerable interest since silver is a metal of value worth recovering from industrial waste waters and low mining liquids [1]. Crown compounds have been shown to form complexes with silver cations [2] and have been used to extract Ag^+ from water into an organic liquid phase [3]. In this respect, stable and lipophilic Ag^+ complexes are most desirable.

From its cation radius, Ag^+ is between the two alkali cations Na^+ and K^+ [4]. Hence it follows that Ag^+ does not match with the cavity of the present macroring **1** which is a 15-crown-5 analogue. Moreover, due to the high number of aromatic/heteroaromatic building blocks, **1** refers to a rather rigid framework with the donor atoms in nearly fixed positions [5]. Nevertheless, a crystalline complex of **1** with $AgNO_3$ was readily obtained. This complex which analysed as a stoichiometric 2:1 complex must be assumed to have an uncommon structure. Therefore we performed an X-ray analysis of the complex $\mathbf{1}\cdot AgNO_3$ (2:1).



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Experimental

Sample preparation and data collection

Stoichiometric amounts of compound **1** [5] and $AgNO_3$ were dissolved in boiling methanol. On slow cooling of the solution, colourless crystals of the title complex, $\mathbf{1}\cdot AgNO_3$ (2:1), formed.

A single crystal of appropriate size 0.1×0.1×0.3 mm was mounted on an Enraf-Nonius CAD-4 diffractometer for three dimensional intensity data collection using graphite monochromatized Mo Kα radiation ($\lambda=0.7107$

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Å) by ω–2θ technique. Cell dimensions and their standard deviations were determined from a least-squares fit of the setting angles for 25 high-angle reflections in the range $20 < 2\theta < 40°$, which had been carefully centred in the counter aperture.

Crystal data

$2(C_{25}H_{19}NO_4) \cdot AgNO_3$, $M_w = 964.73$, triclinic, $P\bar{1}$, $a = 13.182(1)$, $b = 13.612(2)$, $c = 12.720(1)$ Å, $\alpha = 105.39(1)$, $\beta = 99.96(1)$, $\gamma = 103.04(1)°$, $Z = 2$, $T = 295$ K, $D_c = 1.543$ g cm^{-3}, $F(000) = 988.0$, μ(Mo Kα) = 5.46 cm^{-1}. Three standard reflections [$\bar{3}\ \bar{1}\ 4$, $1\ \bar{4}\ 1$ and 2 0 0] were measured after every 100 reflections and their intensities showed deviations of less than 4.8% during the course of data collection. A total of 7210 reflections was measured up to a 2θ value of 60°. A total of 4825 unique reflections with $I \geqslant 3\sigma(I)$ was considered observed and were used in the refinement after applying correction for background, Lorentz and polarization effects and averaging the equivalent reflections [6]. Absorption correction was done using the program ABSORB [7, 8].

Structure solution and refinement

Since the crystal system was confirmed to be triclinic, the space group could be $P1$ or $P\bar{1}$. From the measured density and calculated volume, it was concluded that there were two sandwich complexes in the unit cell and hence the structure may conform to centrosymmetric space group, $P\bar{1}$. The structure solution was tried using the heavy-atom method, since silver is very much heavier than the rest of the atoms present in the structure. A three dimensional Patterson map was computed using SHELX76 [9] to locate the Ag position. The Ag position was deduced from the following Harker peak; the Harker peak with its peak height (relative to the origin peak of 999) is given below:

Peak Ht.	Frac. Coord.	Harker region Vector
681	(0.5, 0.5, 0.5)	plane: $u, v, w \pm (2x, 2y, 2z)$

At this stage, an attempt was made to solve the structure by direct methods using SHELX86 [10]. An E-map analysis with the lowest combined figure of merit of 0.079 leads to the approximate positions of about 90% of the scattering matter. The Ag position obtained from direct methods analysis was in agreement with that obtained from the Patterson map. Successive cycles of least-squares refinement with isotropic temperature factors followed by weighted difference Fourier maps made it possible to complete the structure. The isotropic refinement of non-hydrogen atoms converged at 0.11. At the end of isotropic refinement, the method of Walker and Stuart [8] was applied to correct for the absorption effects using the program ABSORB [7]. The maximum and minimum transmission coefficients were 0.771 and 0.429, respectively. Anisotropic refinement of all the non-hydrogen atoms by full-matrix least-squares method using SHELX76 [9] gave an R value of 0.07. At this stage, all the hydrogen atoms were located from successive difference Fourier maps and were refined isotropically. Individual weights were ascribed according to the scheme $w = k[\sigma^2(F_o) + g|F_o|^2]$ where the final k and g values were 1.7873 and 0.00014, respectively. The refinement was stopped when the maximum shift per e.s.d. for any parameter was less than 0.013 in the final cycle of non-hydrogen refinement. The final R and R_w values were 0.054 and 0.038, respectively. The goodness of fit S was 1.26 for 739 parameters and 4825 reflections. The reflections to parameters refined ratio was about 6.6. The maximum peak height of 0.79 e Å^{-3} in the final difference Fourier map was in the vicinity of silver, and has no chemical significance. The minimum height in the final difference Fourier was -0.86 e Å^{-3}. Atomic scattering factors due to Cromer and Mann [11] for non-hydrogen atoms and of Stewart *et al.* [12] for hydrogen atoms were used. Anomalous dispersion correction terms were taken from ref. 13.

Results and discussion

The final atomic coordinates of the non-hydrogen atoms along with the equivalent isotropic thermal parameters are listed in Table 1; atom labelling is in accordance with Fig. 1. Table 2 shows bond distances of the macroring, Table 3 bond angles. Table 4 gives a selection of torsion angles of the macroring. Bond distances and angles involving Ag are shown in Table 5. The molecular structure of the complex is shown in Fig. 1 and the packing diagram is illustrated in Fig. 2.

Structure of the macroring **1**

Bond parameters

All bond distances (Table 2) and bond angles (Table 3) of the macrocycle **1** are normal or in good agreement with reported values of benzo and pyridino crown compounds [14, 15].

Ring conformation

The conformation of the two macrorings A and B of the sandwich (see Fig. 1) are more or less similar as seen from their respective torsion angles (Table 4). Starting from N(1)–C(2) bond, the macrorings A and B have the conformations $ag^+g^+asaxsg^+asag^-g^-a$ ($x = -114°$) and $ag^-g^-asag^+saasag^+g^+a$, respectively. Thus the torsion codes for A and B are similar except that the order is reversed due to our numbering scheme. As for the individual torsion angles, considerable de-

TABLE 1. Final fractional coordinates and equivalent thermal parameters (Å^2) for the non-hydrogen atoms of $\mathbf{1}\cdot AgNO_3$ (2:1) with e.s.d.s in parentheses

Atom	Macrocycle A				Macrocycle B			
	x/a	*y/b*	*z/c*	U_{eq}	*x/a*	*y/b*	*z/c*	U_{eq}
N1	0.1187(3)	0.3227(3)	0.1874(3)	0.036(2)	0.3887(3)	0.1965(3)	0.2944(3)	0.039(2)
C2	0.0239(3)	0.2586(4)	0.1191(3)	0.036(2)	0.4835(4)	0.2682(4)	0.3502(4)	0.043(2)
C3	0.0029(3)	0.1398(4)	0.1000(4)	0.046(2)	0.4953(3)	0.3802(4)	0.3506(4)	0.053(2)
O4	0.0398(2)	0.1189(2)	0.2017(2)	0.041(1)	0.4415(2)	0.3882(2)	0.2471(3)	0.050(2)
C5	−0.0088(4)	0.1469(3)	0.2881(4)	0.043(2)	0.4870(4)	0.3737(4)	0.1573(4)	0.049(2)
C6	0.0552(4)	0.1676(4)	0.3947(4)	0.051(2)	0.4251(4)	0.3707(3)	0.0554(5)	0.049(2)
O7	0.1608(3)	0.1699(4)	0.3978(3)	0.084(2)	0.3236(3)	0.3861(2)	0.0568(3)	0.052(2)
C8	0.2312(4)	0.1733(4)	0.4950(4)	0.051(3)	0.2375(4)	0.3213(4)	−0.0343(4)	0.048(2)
C9	0.3140(4)	0.2646(4)	0.5445(4)	0.047(3)	0.2078(4)	0.2116(4)	−0.0565(4)	0.052(3)
O10	0.3223(3)	0.3520(3)	0.5065(3)	0.064(2)	0.2628(3)	0.1751(2)	0.0213(3)	0.068(2)
C11	0.2524(4)	0.4124(4)	0.5310(4)	0.052(3)	0.2958(4)	0.0849(4)	−0.0159(4)	0.046(2)
C12	0.2310(3)	0.4719(3)	0.4587(4)	0.038(2)	0.2879(3)	0.0147(3)	0.0426(4)	0.038(2)
O13	0.2825(2)	0.4604(2)	0.3728(2)	0.044(1)	0.2291(2)	0.0316(2)	0.1233(2)	0.039(1)
C14	0.2457(3)	0.4973(3)	0.2818(4)	0.042(2)	0.2686(4)	0.0147(4)	0.2278(4)	0.047(2)
C15	0.1394(4)	0.4280(4)	0.2075(3)	0.039(2)	0.3738(3)	0.0949(4)	0.2948(3)	0.039(2)
C16	0.0652(4)	0.4724(3)	0.1564(4)	0.045(2)	0.4503(4)	0.0671(4)	0.3604(4)	0.045(2)
C17	−0.0275(4)	0.4052(4)	0.0830(4)	0.054(3)	0.5460(4)	0.1425(4)	0.4229(4)	0.052(3)
C18	−0.0497(4)	0.2977(4)	0.0635(4)	0.051(2)	0.5620(4)	0.2422(4)	0.4159(4)	0.056(2)
C19	−0.1141(4)	0.1515(4)	0.2767(4)	0.052(2)	0.5881(4)	0.3599(4)	0.1599(5)	0.065(3)
C20	−0.1546(4)	0.1741(4)	0.3708(5)	0.068(3)	0.6259(5)	0.3496(4)	0.0641(6)	0.073(3)
C21	−0.0913(5)	0.1914(4)	0.4750(5)	0.060(3)	0.5640(5)	0.3488(5)	−0.0341(5)	0.078(4)
C22	0.0132(4)	0.1868(4)	0.4877(4)	0.065(3)	0.4600(5)	0.3595(4)	−0.0398(4)	0.062(3)
C23	0.2278(5)	0.0874(5)	0.5292(5)	0.077(3)	0.1787(5)	0.3667(4)	−0.0963(4)	0.058(3)
C24	0.3109(5)	0.0907(5)	0.6157(5)	0.071(3)	0.0899(5)	0.3020(5)	−0.1803(5)	0.063(3)
C25	0.3949(5)	0.1782(6)	0.6633(4)	0.076(3)	0.0620(5)	0.1960(5)	−0.2042(4)	0.070(3)
C26	0.3982(4)	0.2661(4)	0.6283(4)	0.058(3)	0.1193(5)	0.1489(4)	−0.1419(4)	0.062(3)
C27	0.2127(4)	0.4229(4)	0.6262(4)	0.054(2)	0.3474(4)	0.0732(4)	−0.1038(4)	0.062(3)
C28	0.1497(4)	0.4895(4)	0.6477(4)	0.062(3)	0.3879(4)	−0.0130(5)	−0.1309(4)	0.064(3)
C29	0.1293(4)	0.5476(4)	0.5786(5)	0.063(3)	0.3791(4)	−0.0820(4)	−0.0709(5)	0.060(3)
C30	0.1671(4)	0.5370(4)	0.4833(4)	0.045(2)	0.3271(4)	−0.0723(3)	0.0153(4)	0.047(2)
Ag	0.24771(3)	0.25191(3)	0.23805(3)	0.390(1)				
N2	0.2563(9)	0.7576(7)	0.2544(8)	0.067(4)				
O1	0.2218(7)	0.7195(8)	0.1553(7)	0.157(6)				
O2	0.3508(7)	0.7972(7)	0.2810(9)	0.191(6)				
O3	0.2054(9)	0.7403(7)	0.3161(9)	0.181(8)				

viations from the ideal values [14] are observed. These deviations amount to +40° and reveal that the macrocycles A and B are highly strained. In an ideal macroring conformation, the O–C–C–O torsion angles alternate between g^+ and g^-, while the C–C–O–C angles are all +180° [14]. However, the lower symmetry of the 15-crown-5 macrocycle cannot support the expected ideal conformation since at some point at least two consecutive O–C–C–O torsion angles must have the same sign. Also, one of the torsion angles around a C–O linkage between these two O–C–C–O units is forced to *syn*, although these angles are usually greater than 70° to avoid C–H···H–C repulsion. Consequently, the macrocycle **1** is less likely to adopt a single conformation.

Due to the stiffening of the macrocycle by the benzo units, three of the O–C–C–O groups are constrained to be *syn* thus giving rise to short non-bonded intramolecular O···O interactions in molecules A and B, namely 2.540(4) and 2.630(5) Å for O(4)···O(7), 2.715(5) and 2.691(4) Å for O(7)···O(10), and 2.592(5) and 2.617(5) Å for O(10)···O(13), respectively. In particular the value of 2.540(4) Å is short when compared with the van der Waals O···O non-bonded contact distance of 2.8 Å [16], reflecting the conformational strain in both macrorings. These unfavorable short O···O contacts are compensated by the Ag···O (ion–dipole) interactions in the complex. The heteroatoms N(1), O(4), O(7), O(10) and O(13) are approximately planar in macrocycles A and B, the maximum deviation from planarity being 0.122(4) and 0.279(4) Å, respectively.

The pyridine ring is bent away from the plane of the heteroatoms thereby bringing the direction of the lone pair of electrons in the nitrogen atoms towards the cation. A similar feature was observed in a tri-

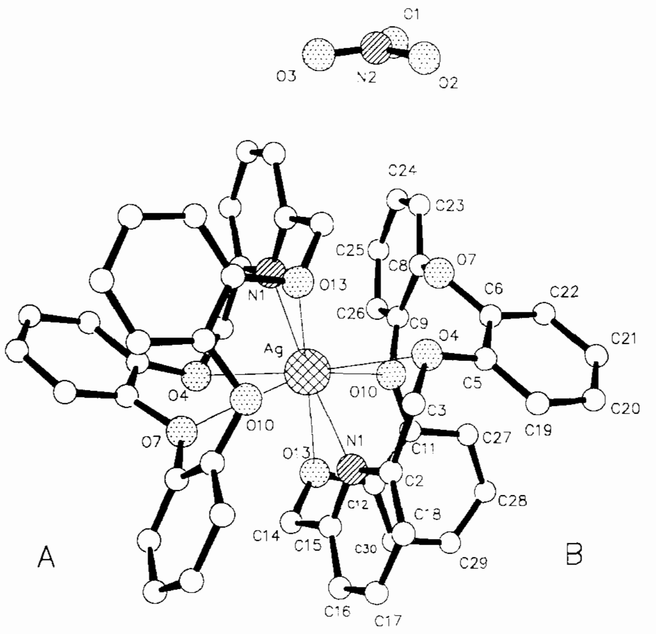

Fig. 1. Perspective view of the sandwich complex $\mathbf{1}\cdot AgNO_3$ including the atom numbering scheme. Heteroatoms are shown by shaded circles, the H atoms are omitted for the sake of clarity.

thiapyridino-12-crown-4 complex with $AgNO_3$ [17]. The conformational strain in the macroring **1** is thus due to the benzo and pyridino condensations and also to the complexing of Ag^+.

Structure of the complex $1\cdot AgNO_3$ (2:1)

Cation coordination

The Ag^+ cation is coordinated to three oxygen atoms and one nitrogen atom (pyridine N) of each macrocycle, namely N(1), O(4), O(7) and O(13) from macroring A and N(1), O(4), O(10) and O(13) from macroring B, thereby being encapsulated in a sandwich cavity of hosts. Using these donors, the Ag^+ cation is eightfold coordinated in a distorted cubic arrangement and is thus completely shielded from the solvent or counter ion interactions. Similar eightfold coordination of Ag^+ was observed in the silver complexes of polyether antibiotics RO 21-6150 [18] and A-130A [19] where the Ag···O coordination distances are less than 3.01 and 3.06 Å, respectively, and in an Ag^+ complex of 12-crown-4 [20]. However, to our knowledge, there is no example of eightfold coordination of Ag^+ in a crown complex involving an N_2O_6 set of donor atoms such as here.

The Ag···O coordination distance in the present complex ranges from 2.736(4) to 2.899(3) Å while the Ag···N coordination distances are 2.219(4) and 2.235(4) Å in molecules A and B, respectively (Table 5). The Ag–N coordination distances are covalent in nature and are significantly less than the sum of their ionic and van der Waals radii (2.96 Å) [16]. These latter contacts are shorter than those observed for other Ag^+ complexes of crown ethers [17, 21] while the Ag···O coordination distances, being greater than the sum of their ionic and van der Waals radii (2.66 Å) [16], are in good agreement with previous reports of antibiotic Ag^+ complexes [14, 22]. The coordination angles at the cation range from 53.4(1) to 174.4(2)° (see Table 5).

The atoms N(1A), O(4A), O(7A), O(13A) and N(1B), O(4B), O(10B), O(13B) are nearly planar with the maximum deviation being −0.044(4) and 0.119(4) Å

TABLE 2. Bond distances (Å) involving non-hydrogen atoms for $\mathbf{1}\cdot AgNO_3$ (2:1) with e.s.d.s in parentheses

Atoms	Distance		Atoms	Distance	
	Macrocycle A	Macrocycle B		Macrocycle A	Macrocycle B
N1–C2	1.344(5)	1.339(5)	N1–C15	1.341(7)	1.354(7)
C2–C3	1.522(8)	1.496(8)	C2–C18	1.386(8)	1.385(8)
C3–O4	1.425(6)	1.427(6)	O4–C5	1.377(6)	1.369(7)
C5–C6	1.387(7)	1.392(8)	C5–C19	1.388(8)	1.383(8)
C6–O7	1.379(7)	1.403(7)	C6–C22	1.379(8)	1.352(9)
O7–C8	1.395(7)	1.400(5)	C8–C9	1.366(6)	1.392(7)
C8–C23	1.346(10)	1.367(9)	C9–O10	1.388(7)	1.388(7)
C9–C26	1.392(7)	1.375(6)	O10–C11	1.388(7)	1.387(7)
C11–C12	1.411(8)	1.355(8)	C11–C27	1.386(8)	1.398(8)
C12–O13	1.376(6)	1.392(6)	C12–C30	1.369(7)	1.382(7)
O13–C14	1.432(6)	1.438(6)	C14–C15	1.490(5)	1.502(5)
C15–C16	1.414(8)	1.380(7)	C16–C17	1.360(6)	1.383(6)
C17–C18	1.370(8)	1.355(8)	C19–C20	1.383(8)	1.380(10)
C20–C21	1.368(8)	1.365(10)	C21–C22	1.377(9)	1.403(10)
C23–C24	1.395(9)	1.375(7)	C24–C25	1.342(8)	1.341(9)
C25–C26	1.378(10)	1.375(9)	C27–C28	1.369(8)	1.383(9)
C28–C29	1.361(9)	1.357(10)	C29–C30	1.374(9)	1.383(9)

TABLE 3. Bond angles (°) involving non-hydrogen atoms for $\mathbf{1}\cdot AgNO_3$ (2:1) with e.s.d.s in parentheses

Atoms	Angle		Atoms	Angle	
	Macrocycle A	Macrocycle B		Macrocycle A	Macrocycle B
C2–N1–C15	118.8(4)	118.9(4)	N1–C2–C18	121.8(5)	121.0(5)
N1–C2–C3	117.2(4)	117.1(4)	C3–C2–C18	120.9(4)	121.4(5)
C2–C3–O4	111.4(4)	113.7(4)	C3–O4–C5	118.0(3)	119.8(4)
O4–C5–C19	126.1(4)	125.1(5)	O4–C5–C6	114.6(5)	116.9(5)
C6–C5–C19	119.2(5)	118.1(5)	C5–C6–C22	120.5(5)	123.7(6)
C5–C6–O7	114.6(4)	116.2(5)	O7–C6–C22	124.9(5)	120.1(5)
C6–O7–C8	121.6(4)	117.4(4)	O7–C8–C23	122.4(5)	119.7(5)
O7–C8–C9	115.7(5)	119.8(4)	C9–C8–C23	121.2(5)	120.3(5)
C8–C9–C26	118.7(5)	119.6(5)	C8–C9–O10	122.2(5)	115.7(5)
O10–C9–C26	118.8(5)	124.2(5)	C9–O10–C11	117.1(4)	119.6(4)
O10–C11–C27	123.0(5)	120.3(5)	O10–C11–C12	116.1(4)	118.6(4)
C12–C11–C27	120.6(5)	120.7(5)	C11–C12–C30	118.1(4)	121.4(5)
C11–C12–O13	114.5(4)	115.0(4)	O13–C12–C30	127.4(4)	123.4(4)
C12–O13–C14	117.3(3)	117.0(3)	O13–C14–C15	112.9(4)	112.3(4)
N1–C15–C14	117.9(5)	118.1(4)	C14–C15–C16	120.5(4)	120.8(5)
N1–C15–C16	121.6(4)	121.0(5)	C15–C16–C17	118.3(4)	120.0(5)
C16–C17–C18	120.3(5)	118.1(5)	C2–C18–C17	119.0(5)	120.8(5)
C5–C19–C20	119.9(5)	119.2(5)	C19–C20–C21	120.2(5)	121.3(6)
C20–C21–C22	120.7(5)	120.5(6)	C6–C22–C21	119.5(5)	117.1(5)
C8–C23–C24	119.6(6)	118.7(5)	C23–C24–C25	120.4(6)	121.5(6)
C24–C25–C26	119.9(6)	120.7(6)	C9–C26–C25	120.1(5)	119.2(5)
C11–C27–C28	119.2(5)	118.3(5)	C27–C28–C29	120.4(5)	119.9(5)
C28–C29–C30	120.9(5)	122.6(5)	C12–C30–C29	120.7(5)	117.2(4)

TABLE 4. Selected torsion angles (°) of $\mathbf{1}\cdot AgNO_3$ (2:1) with e.s.d.s in parentheses

Atoms	Angle	
	Macrocycle A	Macrocycle B
C2–N1–C15–C14	−178.9(4)	−177.5(4)
C15–N1–C2–C3	−179.1(4)	−178.1(4)
N1–C2–C3–O4	40.9(6)	−36.8(6)
C2–C3–O4–C5	64.1(5)	−78.3(5)
C3–O4–C5–C6	−153.8(4)	173.0(4)
O4–C5–C6–O7	7.8(7)	1.8(7)
C5–C6–O7–C8	−170.0(5)	−138.4(5)
C6–O7–C8–C9	−113.6(6)	61.6(6)
O7–C8–C9–O10	5.5(8)	4.8(7)
C8–C9–O10–C11	74.1(7)	−138.4(5)
C9–O10–C11–C12	−155.9(5)	−140.6(5)
O10–C11–C12–O13	0.6(6)	11.0(7)
C11–C12–O13–C14	165.6(4)	−141.2(4)
C12–O13–C14–C15	−72.3(5)	67.1(5)
O13–C14–C15–N1	−36.9(6)	37.8(6)

TABLE 5. Bond distances (Å) and angles (°) involving Ag for $\mathbf{1}\cdot AgNO_3$ (2:1) with e.s.d.s in parentheses

Distances		Angles	
Ag–N1A	2.219(4)	N1A–Ag–N1B	174.32(2)
Ag–O4A	2.807(4)	N1A–Ag–O13A	66.4(2)
Ag–O7A	2.850(4)	N1A–Ag–O4A	66.5(2)
Ag–O13A	2.786(4)	O4A–Ag–O7A	53.4(2)
Ag–N1B	2.235(4)	O7A–Ag–O13B	84.4(2)
Ag–O4B	2.762(4)	N1B–Ag–O10B	88.5(2)
Ag–O10B	2.736(4)	O4B–Ag–O10B	79.3(2)
Ag–O13B	2.899(4)	O4B–Ag–O13A	66.1(2)
		N1B–Ag–O13B	64.9(2)

from their respective planes. These planes are approximately parallel, the dihedral angle between them is 5.7°. These planes form the opposite faces of the cube and the distance between them is approximately 3 Å. The Ag^+ cation sits nearly at the midway point between the planes. The Ag^+ cation of 2.52 Å in diameter is thus entrapped in a hydrophilic cavity of appropriate size. On the other hand, the exterior of the sandwich complex is highly hydrophobic since all the CH_2 and aromatic groups point outwards.

Anion structure and interaction

The nitrate anion does not interact with the capsulated Ag^+ cation. The shortest distance between Ag^+ and NO_3^- is 6.62(1) Å. The nitrate group is planar with the maximum deviation being −0.06(2) Å, and the Ag^+ is displaced by about 6.563(1) Å above the plane formed by the nitrate group (Fig. 1). However, the nitrate anion is involved in a $C\text{–}H\cdots O$ type of interaction [23, 24]. Significant cases are: (i) $C(14A)\cdots O(3) = 3.397(11)$ Å, $C(14A)\text{–}H(3A)\cdots O(3) = 164(10)°$; (ii) $C(21A)\cdots O(3) = 3.309(14)$ Å,

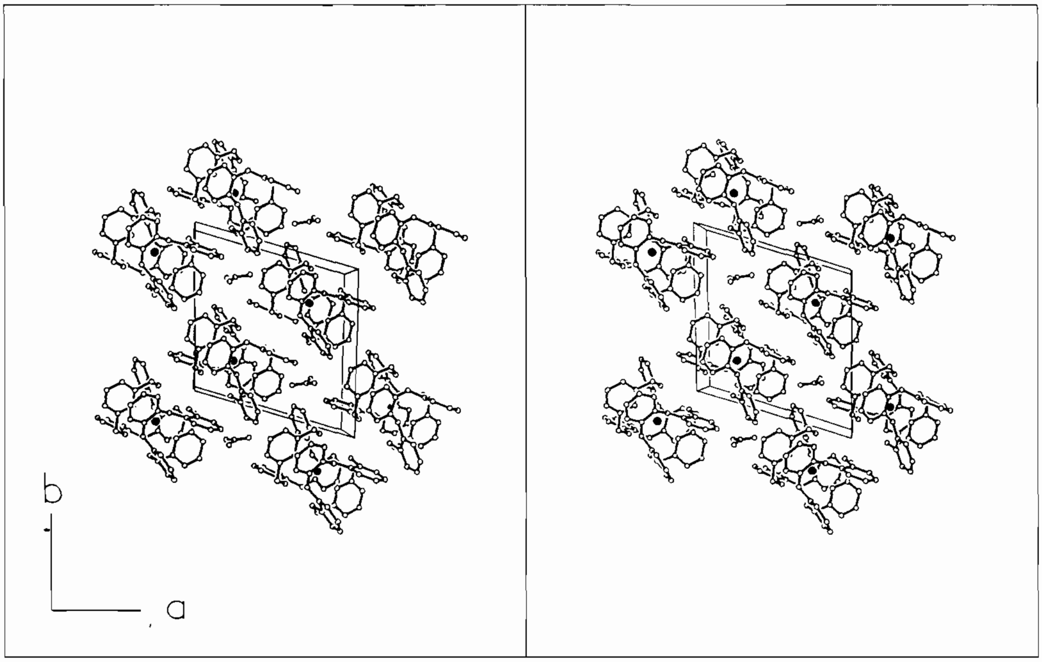

Fig. 2. Crystal packing of the **1**·$AgNO_3$ (2:1) complex (stereoview down the *c* axis). The silver cation is indicated as a bold dot.

C(21A)–H(10A)···O(3) = 162(9)°; (iii) C(16B)···O(2) = 3.393(10) Å, C(16B)–H(5B)···O(2) = 163(9)°.

Figure 2 shows the stereoview of the molecular packing in the unit cell. There is no noticeable packing feature in the crystal lattice such as stacking of the pyridine rings which is frequently seen for pyridino crowns [15, 17, 25]. Therefore, the structure of the present complex can be best described as comprising rather discrete $[(crown)_2Ag^+]$ cations and NO_3^- anions packed in a van der Waals mode and stabilized by some CH···O type of interactions.

Conclusions

As expected from ion radius–cavity concept, Ag^+ forms a sandwich complex with tribenzopyridino-15-crown-5 (**1**) where the cation is completely shielded from the counter ion interaction. As an unparalleled example of a crown–Ag^+ complex, the Ag^+ is eightfold coordinated in a distorted cubic arrangement of two N and six O atoms. The Ag^+ is entrapped in a hydrophilic cavity of approximately 3 Å diameter while the exterior of the complex is highly hydrophobic, thus fulfilling the requirements for an effective trans-membrane transport [26] and for efficient solvent extraction [27] of silver salts which are important processes for the regeneration of Ag^+ from industrial waste waters. Ag^+ complexed in a closed organic shell is also promising in the photographic field [28].

Supplementary material

Least-squares planes through various groups of atoms, thermal parameters, hydrogen positions, bond lengths and angles involving hydrogen atoms, and observed and calculated structure factors are available from the authors on request.

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