

A pseudo-cage complex of silver(I) with tripodal tetraamine having benzyl end groups, {tris[2-(benzylamino)-ethyl]amine- κ^4N }silver(I) perchlorate

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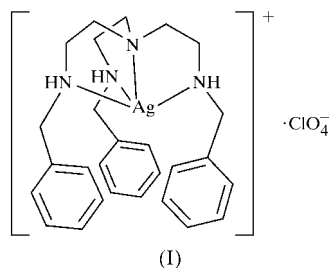
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The synthesis and crystal structure of {tris[2-(benzylamino)-ethyl]amine- κ^4N }silver(I) perchlorate, [Ag(C₂₇H₃₆N₄)]ClO₄ or [Ag(bz₃tren)]ClO₄ {bz₃tren is tris[2-(benzylamino)ethyl]amine or N,N',N''-tribenzyltris(2-aminoethyl)amine} are reported. The Ag atom is coordinated to four N atoms of the tren unit and is located 0.604 (3) Å out of the trigonal plane described by the three secondary amine N atoms, away from the bridgehead N atom. Edge-to-face π - π interactions between the aromatic end groups, and weak interactions between Ag and arene, allow the formation of a pseudo-cage complex.

Comment

Tripodal complexes with transition metals have been widely investigated. The ligands used most in this area have been tren, the tripodal tetraamine N(CH₂CH₂NH₂)₃, and its derivatives (Zipp *et al.*, 1974). Many cage complexes, such as bimetallic complexes with bis(tren) cryptands, have also been



reported (Amendola *et al.*, 2001). Acyclic ionophores with aromatic end groups, so-called podands, sometimes form unusual pseudo-cyclic complexes with alkali or soft metal ions *via* intramolecular π - π interactions between two aromatic end groups (Weber & Saenger, 1979). However, tripodal pseudo-cage complexes formed by π - π interactions between aromatic

end groups have not yet been reported. As part of our continuing studies (Lee *et al.*, 1995; Chung *et al.*, 1997) involving such multipodal ligands and their pseudo-cyclic complexes, the present ligand was chosen with this aspect in mind. We report herein our result in this area, with the crystal structure of {tris[2-(benzylamino)ethyl]amine- κ^4N }silver(I) perchlorate, [Ag(bz₃tren)]ClO₄, (I).

As shown in Fig. 1, the Ag atom in (I) is coordinated to the bridgehead N atom (N_{br}) and to three secondary amino N atoms (N2, N3 and N4). Upon complexation, the tren unit becomes quite rigid and maintains the *endo* conformation, with the N_{br} atom displaced by 0.387 (6) Å towards the Ag atom above the triangular plane through atoms C1, C10 and C19. The N1-C-C-N torsion angles are in the range 61.1 (6)–62.5 (6)°, suggesting *gauche* conformations. The Ag atom is displaced by 0.604 (3) Å out of the trigonal plane described by the three secondary amines, away from the N_{br} atom. The Ag–N_{br} bond [2.507 (5) Å] is at the upper end of the range for Ag–N_{br} (Ferguson *et al.*, 1989; Adam *et al.*, 1995), and is significantly longer than the other Ag–N bonds in (I) [2.350 (3)–2.362 (3) Å]. Selected geometric parameters and the hydrogen-bonding geometry are listed in Tables 1 and 2, respectively.

The potential threefold symmetry of the complex cation in (I) is broken by the non-coordinating ClO₄[−] ion and the three less well aligned aromatic end groups. The three aromatic rings are essentially planar and lie nearly perpendicular to each other, displaying dihedral angles of 73.1 (2), 67.0 (2) and 65.7 (2)°. This permits weak edge-to-face π - π interactions between the aromatic end groups, with a distance from atom C9 to the centroid of the neighbouring C22–C27 ring of 3.856 (8) Å, from atom C14 to the centroid of the neighbouring C4–C9 ring of 3.962 (8) Å and from atom C23 to the centroid of the neighbouring C13–C18 ring of 3.989 (8) Å.

The principal distortion of the coordination sphere arises from the shift of the Ag atom out of the trigonal plane. The

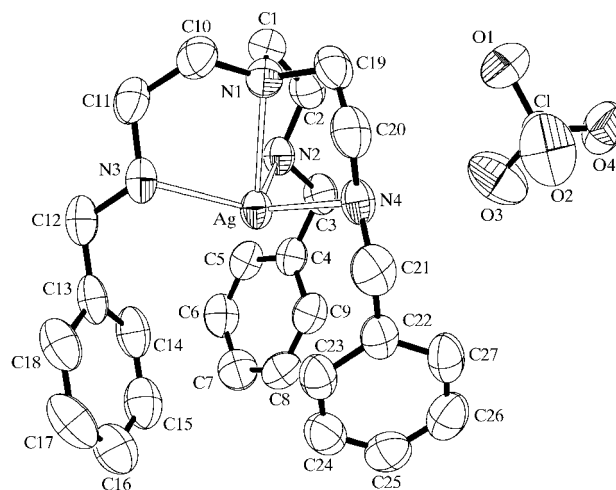


Figure 1
A perspective view of compound (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

shortest Ag \cdots C_{arene} distance is 3.383 (6) Å, well outside the normal Ag \cdots π interaction range (2.47–2.76 Å; Munakata *et al.*, 1998). The shift of the Ag atom towards the aromatic end groups, and the elongation of the Ag–N_{br} bond, which is about 0.15 Å longer than the other Ag–N bonds, may reflect, at least in part, the presence of an additional long-range Ag \cdots arene interaction (Galka & Gade, 1999).

The π – π interactions between the benzyl end groups, and the partial contribution of the weak Ag \cdots arene interactions, allow little room for anion or solvent, which usually coordinates to a metal centre to give the five-coordinate geometry normally observed in tripodal ligands of similar structures.

Experimental

The ligand was synthesized according to the procedure published by Ibrahim *et al.* (2001), with slight modifications. To a solution containing bz₃tren in acetonitrile was added a solution of an equimolar amount of silver perchlorate dissolved in acetonitrile. Slow evaporation of the resulting solution in the dark afforded colourless crystals of (I) suitable for X-ray crystallographic analysis.

Crystal data

[Ag(C ₂₇ H ₃₆ N ₄)]ClO ₄	$D_x = 1.420 \text{ Mg m}^{-3}$
$M_r = 623.92$	Mo $K\alpha$ radiation
Monoclinic, Cc	Cell parameters from 9303 reflections
$a = 16.0287 (11) \text{ \AA}$	$\theta = 2.2\text{--}28.3^\circ$
$b = 9.6132 (7) \text{ \AA}$	$\mu = 0.82 \text{ mm}^{-1}$
$c = 20.2697 (15) \text{ \AA}$	$T = 296 (2) \text{ K}$
$\beta = 110.906 (1)^\circ$	Block, colourless
$V = 2917.7 (4) \text{ \AA}^3$	$0.5 \times 0.4 \times 0.4 \text{ mm}$
$Z = 4$	

Data collection

Siemens SMART CCD area-detector diffractometer	4068 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.026$
9303 measured reflections	$\theta_{\text{max}} = 28.3^\circ$
3627 independent reflections (plus 1637 Friedel-related reflections)	$h = -15 \rightarrow 21$
	$k = -12 \rightarrow 11$
	$l = -26 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.2006P]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.090$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.99$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
5264 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
334 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.02 (3)

H atoms were added at calculated positions, with C–H = 0.96 Å and N–H = 0.90 Å, and refined using a riding model, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent atom.

Table 1

Selected geometric parameters (Å, °).

Ag–N4	2.353 (3)	Ag–N3	2.362 (3)
Ag–N2	2.350 (3)	Ag–N1	2.507 (5)
N4–Ag–N2	111.22 (13)	N4–Ag–N1	75.34 (14)
N4–Ag–N3	114.19 (13)	N2–Ag–N1	75.27 (14)
N2–Ag–N3	115.53 (13)	N3–Ag–N1	74.79 (13)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N4–H4 \cdots O3	0.90	2.58	3.481 (8)	179

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SHELXTL (Siemens, 1996); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1051). Services for accessing these data are described at the back of the journal.

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