Co-ordination Chemistry of 1,4,7-Triazacyclononane (L) and its N-Methylated Derivative (L′) with Silver(I) and Mercury(II). The Crystal Structures of $[AgL'_2]PF_6$ and $[AgL'(SCN)]$†

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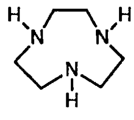
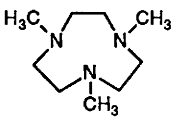
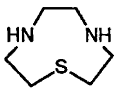
Reaction of $AgPF_6$ in acetonitrile with an equimolar amount of the macrocycle 1,4,7-triazacyclononane (L) and addition of $[NBu_4]X$ (X = Cl, Br, I or CN) affords colourless to yellow precipitates of $[AgL(X)]$. The complexes $[AgL'(X)]$ (X = SCN or CN) (L′ = 1,4,7-trimethyl-1,4,7-triazacyclononane) have been prepared similarly. When the ligand to $AgPF_6$ ratio was 2:1 in ethanolic solution, colourless crystals of $[AgL_2]PF_6$ and $[AgL'_2]PF_6$ were obtained, respectively. A binuclear species $[LAg(\mu\text{-}CN)AgL]PF_6$ has been obtained from a solution of $AgPF_6$ and L (1:1) in pyridine upon addition of NaCN (0.5 equivalent). Mercury(II) chloride reacts in water with L (1:2) and addition of $NaPF_6$ to yield $[HgL_2][PF_6]_2$; with L′ the complex $[HgL'(Cl)]PF_6$ was obtained. Crystals of $[AgL'_2]PF_6$ are tetragonal, space group *P*4$_2$/*m* (no. 84), with *a* = 10.134(1), *c* = 12.771(2) Å, and *Z* = 2. Crystals of $[AgL'(SCN)]$ are orthorhombic, space group *Pcmn* (no. 62), with *a* = 9.497(5), *b* = 11.837(8), *c* = 26.00(1) Å and *Z* = 8.

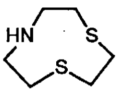
The co-ordination chemistry of tridentate nine-membered cyclic ligands containing nitrogen and sulphur donor atoms such as those denoted as L,L′ and L^1–L^5 has in the past decade been thoroughly investigated.[1] These ligands are ideally suited to co-ordinate facially to three sites of an octahedron. Only in a few instances have other co-ordination polyhedra been capped by these ligands (*e.g.* a tetrahedron).[1] The thermodynamic and kinetic stability of complexes containing these ligands frequently exceeds those of their open-chain analogues.

Here we report the synthesis and two crystal structures of complexes of 1,4,7-triazacyclononane (L) and its *N*-methylated derivative 1,4,7-trimethyl-1,4,7-triazacyclononane (L′) with silver(I) and mercury(II). Macrocyclic thioether complexes of these soft metal ions[2,3] have been investigated but not their aza analogues. Parker and co-workers[4,5] have recently reported on some complexes of Ag^I containing the N,S macrocycles L^2, L^3 and L^5.


L


L′


L^1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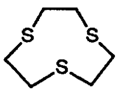
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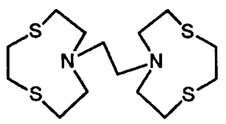
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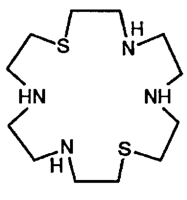
L^5

Results and Discussion

Synthesis of Complexes.—Silver hexafluorophosphate dissolved in acetonitrile reacts at 25 °C in the absence of light with the macrocyclic ligand 1,4,7-triazacyclononane (L) in a 1:1 ratio forming the fragment LAg^+. In the presence of uninegatively charged anions, which were added as tetrabutylammonion salts $[NBu_4]X$ (X = Cl, Br or I), the neutral species $[AgL(X)]$ precipitate as white to light yellow solids which are insoluble in all common solvents. In the light of the X-ray crystal-structure determinations of $[CuL^3(I)]^{2a}$ and $[AgL'[(SCN)]$ we propose a pseudo-tetrahedral ligand environment for the Ag^I in these materials. In the infrared spectrum (KBr discs) a single ν(N–H) stretching frequency is observed at 3240 cm^{-1} which is in accord with the above proposal.

When solid NaCN was added to the above reaction mixture instead of $[NBu_4]X$ salts the corresponding complex $[AgL(CN)]$ was isolated as a white microcrystalline solid. The infrared spectrum of this material exhibits a ν(CN) stretching frequency at 2100 cm^{-1}. The analogous complex $[AgL'(CN)]$ containing the *N*-methylated derivative of L was prepared similarly; the ν(CN) frequency is observed at 2116 cm^{-1}. Both

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† Bis(1,4,7-trimethyl-1,4,7-triazacyclononane-κ^3*N*^{1},*N*^{4},*N*^{7})silver(I) hexafluorophosphate and (thiocyanato-κ*S*)(1,4,7-trimethyl-1,4,7-triazacyclononane-κ^3*N*^{1},*N*^{4},*N*^{7})silver(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

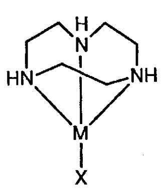

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Complex **1**			
Ag–N(1)	2.543(10)	Ag–N(2)	2.607(7)
N(1)–C(1)	1.445(15)	N(1)–C(4)	1.495(18)
N(2)–C(2)	1.446(14)	N(2)–C(3)	1.468(12)
N(2)–C(5)	1.455(12)	C(1)–C(2)	1.351(19)
C(3)–C(3a)	1.345(13)		
N(1)–Ag–N(1a)	180.0(5)	N(1)–Ag–N(2)	71.6(3)
N(1)–Ag–N(2a)	108.4(3)	N(2)–Ag–N(2a)	180.0(4)
N(2)–Ag–N(2b)	111.2(2)	N(2)–Ag–N(2c)	68.8(2)
Complex **2**			
Ag(1)–S(1)	2.360(4)	Ag(2)–S(11)	2.368(5)
Ag(1)–N(2)	2.413(11)	Ag(2)–N(12)	2.350(10)
Ag(1)–N(3)	2.399(8)	Ag(2)–N(13)	2.431(12)
S(1)–C(1)	1.619(23)	S(11)–C(11)	1.605(21)
N(1)–C(1)	1.115(30)	N(11)–C(11)	1.196(28)
S(1)–Ag(1)–N(2)	131.5(3)	S(11)–Ag(2)–N(12)	137.8(3)
S(1)–Ag(1)–N(3)	137.7(2)	S(11)–Ag(2)–N(13)	131.1(3)
N(2)–Ag(1)–N(3)	73.9(3)	N(12)–Ag(2)–N(13)	74.7(3)
S(1)–Ag(1)–N(3a)	137.7(2)	S(11)–Ag(2)–N(12a)	137.8(3)
N(2)–Ag(1)–N(3a)	73.9(3)	N(12)–Ag(2)–N(12a)	74.2(5)
N(3)–Ag(1)–N(3a)	75.1(4)	N(13)–Ag(2)–N(12a)	74.7(3)
Ag(1)–S(1)–C(1)	98.9(7)	Ag(2)–S(11)–C(11)	100.0(7)
S(1)–C(1)–N(1)	174.8(19)	S(11)–C(11)–N(11)	179.2(12)

[AgL(CN)] and [AgL′(CN)] are soluble in methanol. The ^{13}C NMR spectrum of the latter was recorded in [^{2}H$_4$ methanol]: δ 49.6 (CH_3), 55.5 (CH_2) and 147.1 (CN). The resonance of unco-ordinated CN^- is observed at δ 169.

A suspension of freshly prepared AgSCN in MeCN reacts with 1 equivalent of L′ in the absence of light at room temperature generating a clear solution from which colourless crystals of [AgL′(SCN)] precipitated within 12 h at 10 °C. In the infrared spectrum a ν(CN) frequency is observed at 2094 cm^{-1} which indicates an S-co-ordinated thiocyanate. The ^{13}C NMR spectrum measured in $CDCl_3$ exhibits resonances at δ 49.0 (CH_3), 55.5 (CH_2) and 124.2 (SCN). The crystal structure (see below) confirms the tetrahedral N_3S environment of the Ag^I.

Interestingly, the reaction of the LAg$^+$ fragment and CN^- in ratio 2:1 in pyridine and addition of $NaPF_6$ produces a white solid material which analyses as Ag:L:CN:PF_6 2:2:1:1 in agreement with a dinuclear μ-cyano bridged species [LAg–CN–AgL]PF_6. The ν(CN) stretching frequency is observed at 2140 cm^{-1}. This shift to higher frequencies as compared to [AgL(CN)] is usually observed on going from monodentate terminal to bridging cyanide ligation.[6]

When the ratio of the macrocyclic amine ligand to $AgPF_6$ was raised to 2:1 in ethanolic solution the hexafluorophosphate salts of the cations $[AgL_2]^+$ and $[AgL'_2]^+$, respectively, precipitated in the absence of light at room temperature. The ^{1}H NMR spectrum of $[AgL'_2]PF_6$ (CD_3CN) exhibits two resonances at δ 2.5 (9 H, CH_3) and 2.6 (6 H, CH_2), and the ^{13}C NMR spectrum shows two signals at δ 48.9 (CH_3) and 55.0 (CH_2). The compounds $[AgL_2]PF_6$ and $[AgL'_2]PF_6$ are light-sensitive and soluble in water, methanol, ethanol and MeCN. Numerous pseudo-octahedral bis(1,4,7-triazacyclononane)-metal-(II) and -(III) complexes have been prepared and crystallographically characterized[1] but $[AgL'_2]^+$ represents the first example of this kind with the sterically demanding 1,4,7-trimethyl-1,4,7-triazacyclononane ligand. In general, the bulky methyl groups prevent the formation of $[ML'_2]^{n+}$ species. Only cations with a large effective ionic radius appear to be able to form this type of complex. This is nicely borne out by the fact that Ag^I does form this complex (effective ionic radius[7] of Ag$^+$ with a co-ordination number six is 1.15 Å), whereas up to now Hg^{2+} does not (effective ionic radius of Hg^{2+} 1.02 Å). Mercury(II) chloride dissolved in water was found to react with L and L′ generating upon addition of $NaPF_6$ white microcrystalline precipitates of $[HgL_2]PF_6$ and $[HgL'(Cl)]PF_6$. Under these conditions $[HgL'_2]^+$ does not form even when using a large excess of L′.

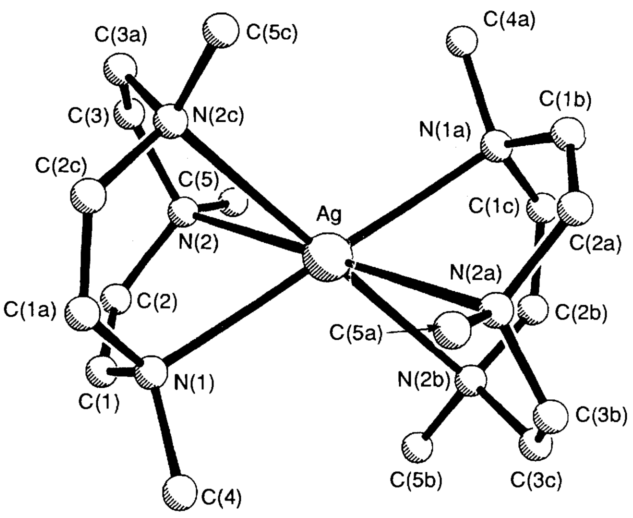

Fig. 1 Structure of the cation $[AgL'_2]^+$ in a crystal of **1**

Crystal Structures.—$[AgL'_2]PF_6$ **1**. Crystals of this complex consist of the cation $[AgL'_2]^+$ and discrete PF_6 anions. Fig. 1 shows the cation and the atom labelling scheme; selected bond distances and angles are given in Table 1. The silver(I) ion is in a pseudo-octahedral environment comprised of two 1,4,7-trimethyl-1,4,7-triazacyclononane ligands (N_6-donor set). The Ag–N distances range from 2.54(1) to 2.607(7) Å; they are rather long but agree well with those in Parker's complexes $[AgL^3]^+$ [2.586(3) Å][4] and $[AgL^5]^+$ [2.589(10), 2.553(11) Å].[5] As a consequence of these long distances the intraligand N–Ag–N bond angles at 70° are small whereas the corresponding interligand N–Ag–N angles at ≈109° are large. The cation possesses crystallographic site symmetry 2/*m* which is not compatible with a (λλλ) or (δδδ) configuration of the nine-membered ring of the co-ordinated macrocycle. Consequently, the methylene carbon atoms are disordered and the C–C distances are physically meaningless. The cation $[AgL'_2]^+$ is the first crystallographically characterized example of a bis(1,4,7-trimethyl-1,4,7-triazacyclononane)metal complex. The six bulky methyl groups of the two ligands are staggered.

[AgL′(SCN)] **2**. Crystals of complex **2** consist of pairwise packed [AgL′(SCN)] molecules (Fig. 2). The silver(I) ion is in a tetrahedral environment composed of the tridentate cyclic amine and an S-co-ordinated thiocyanate. The average Ag–N bond distance of 2.387 Å is shorter by ≈0.20 Å than in the octahedral complex $[AgL'_2]PF_6$. The difference in the effective ionic radii between octahedrally and tetrahedrally co-ordinated Ag^I is ≈0.15 Å.[7] The steric crowding of the six methyl groups in $[AgL'_2]^+$ obviously leads to some lengthening of the Ag–N bonds. In the recently characterized tetrahedral complex $[Ag\{Me_2C(pz)_2\}_2ClO_4$,[8] where $Me_2C(pz)_2$ represents the didentate N-donor ligand 2,2′-bis(pyrazol-1-yl)propane, the average Ag–N distance is 2.323 Å indicating some π-acceptor properties of the pyrazolyl moiety.

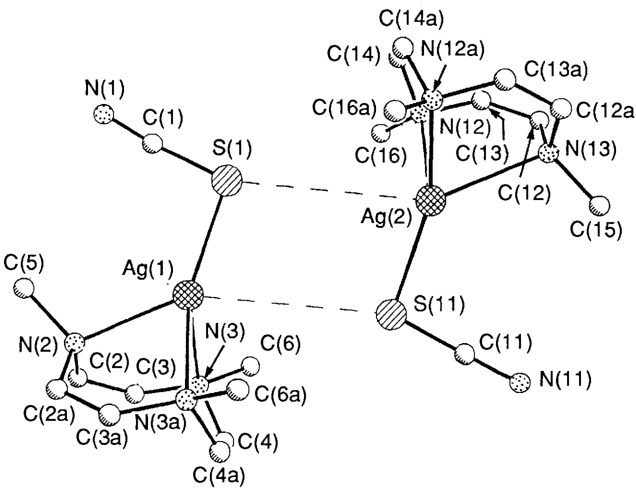

Fig. 2 Structure of a pair of [AgL′(SCN)] molecules in a crystal of **2**

As indicated above in crystals of complex **2** the [AgL′(SCN)] molecules are packed pairwise. The sulphur and silver atoms form a planar four-membered ring of rhomboidal shape with two short Ag(1)–S(1) and Ag(2)–S(11) bond distances at 2.360(4) and 2.368(5) Å and two very long distances Ag(1) ··· S(11) and Ag(2) ··· S(1) at 3.948(8) and 3.959(8) Å, respectively. The latter distances are too long for a bonding interaction between silver(I) and sulphur and, therefore, the observed arrangement of [AgL′(SCN)] molecules is considered to be a crystal-packing effect rather than a weak bonding interaction leading to genuine dimers. It is noted that a pair has approximately $2/m$ point symmetry which is not a crystallographic site symmetry in the space group *Pcmn*.

Experimental

The macrocycles 1,4,7-triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane were prepared as described previously.[9]

Preparation of Complexes.—[AgL(X)] (X = Cl, Br, I or CN). To a solution of $AgPF_6$ (1 mmol) and 1,4,7-triazacyclononane (1.2 mmol) in acetonitrile (20 cm^3) was added tetrabutylammonium halide ($[NBu_4]X$; X = Cl, Br or I) (1.5 mmol) at room temperature with strict protection from light. Colourless (Cl) to yellow (I) precipitates formed within a few hours which were filtered off, washed with diethyl ether and air-dried (yields: 60–80% based on $AgPF_6$). The complex [AgL(CN)] was prepared similarly by addition of NaCN (1 mmol) instead of a $[NBu_4]X$ salt to the above solution (yield: 57%). All [AgL(X)] compounds are light-sensitive and were stored in the dark. The complex [AgL(Cl)] was also prepared by adding the ligand L (1 mmol) to a suspension of freshly precipitated AgCl (1 mmol) in MeCN (20 cm^3) and heating to reflux for 3.5 h.

$[AgL_2]PF_6$ and $[AgL'_2]PF_6$. To a solution of $AgPF_6$ (1 mmol) in dry ethanol (50 cm^3) was added L and L′ (2.3 mmol), respectively, with stirring at room temperature in the dark. Within a few minutes white precipitates formed which were filtered off, washed with diethyl ether and air-dried (yields: ≈90%). Single crystals of $[AgL'_2]PF_6$ suitable for an X-ray structure determination were grown from a mixture of $[AgL'_2]PF_6$ in cyclohexane to which CH_2Cl_2 was added dropwise at 20 °C until a clear solution was obtained. Within 24 h at 0 °C translucent colourless crystals formed.

$[LAg(\mu\text{-}CN)AgL]PF_6$. To a solution of $AgPF_6$ (1 mmol) and L (1.2 mmol) in pyridine (50 cm^3) was added solid NaCN (0.5 mmol). After stirring the solution at 40 °C for 1 h addition of dry diethyl ether (50 cm^3) initiated the precipitation of a colourless microcrystalline solid which was filtered off and washed with diethyl ether and air-dried (yield: 40%).

Table 2 Microanalytical data (%) for the complexes *

Complex	C	H	N
[AgL(Cl)]	26.5 (26.4)	5.5 (5.6)	14.8 (15.4)
[AgL(Br)]	22.9 (22.7)	4.8 (4.7)	13.0 (13.3)
[AgL(I)]	19.9 (19.8)	4.3 (4.2)	11.7 (11.5)
$[AgL_2]PF_6$	27.7 (28.2)	6.2 (5.9)	16.2 (16.4)
$[AgL'_2]PF_6$	36.3 (36.0)	7.1 (6.9)	14.1 (13.9)
$[LAg(\mu\text{-}CN)AgL]PF_6$	25.2 (24.2)	4.8 (4.7)	15.7 (15.2)
[AgL′(SCN)]	36.1 (35.6)	5.9 (6.2)	16.5 (16.6)
[AgL′(CN)]	38.7 (39.4)	6.9 (6.9)	18.4 (18.4)
$[HgL_2][PF_6]_2$	19.3 (19.2)	4.3 (4.1)	10.9 (11.2)
$[HgL'(Cl)]PF_6$	20.5 (19.6)	4.3 (3.9)	8.2 (7.6)

* Required values are given in parentheses.

Table 3 Crystallographic data[a] for $[AgL'_2]PF_6$ and [AgL′(SCN)]

Complex	$[AgL'_2]PF_6$	[AgL′(SCN)]
Formula	$C_{18}H_{42}AgF_6N_6P$	$C_{10}H_{21}AgN_4S$
M	595.43	337.25
Crystal dimensions/mm	0.13 × 0.16 × 0.20	0.15 × 0.20 × 0.80
Diffractometer	Nicolet R3m/V	Syntex R3
Space group	$P4_2/m$ (no. 84)	*Pcmn* (no. 62)
Crystal system	Tetragonal	Orthorhombic
a/Å	10.134(1)	9.497(5)
b/Å		11.837(8)
c/Å	12.771(2)	26.00(1)
U/Å^3	1311.6	2922.8
Z	2	8
D_c/g cm^{-3}	1.507	1.53
μ(Mo-Kα)/mm^{-1}	0.88	1.49
2θ range/°	$3 \leqslant 2\theta \leqslant 55$	$3 \leqslant 2\theta \leqslant 60$
Scan method	ω–2θ	ω
Transmission coefficients	0.652–0.678	0.796–0.867
Total data collected	3411	4827
Independent data [$I > 2.5\sigma(I)$]	905	1951
Total variables	81	164
R^b	0.060	0.079
R'^b	0.047	0.069
Residual electron density/e Å^{-3}	0.82	0.95

[a] Details in common: colour, white; Mo-Kα radiation (λ = 0.710 73 Å). [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ with weights $w = \sigma_F^{-2}$.

[AgL′(SCN)]. To a suspension of freshly prepared AgSCN (1 mmol) in MeCN (50 cm^3) was added L′ (1.2 mmol) with stirring at room temperature. The reaction vessel was protected from light. From the clear solution colourless crystals precipitated within 12 h at 10 °C (yield: 40%) which were found to be suitable for an X-ray structure determination. The crystals are light-sensitive.

[AgL′(CN)]. To a solution of $AgNO_3$ (1 mmol) and L′ (1.2 mmol) in MeCN (50 cm^3) was added NaCN (1 mmol) at room temperature in the absence of light. After 2 h of stirring a white precipitate had formed which was filtered off (yield: 50%). The product is soluble in methanol and not light sensitive.

$[HgL_2][PF_6]_2$. A solution of $HgCl_2$ (1 mmol) and L (2.3 mmol) in water (50 cm^3) was heated under reflux for 2 h. To the colourless solution was added $NaPF_6$ (1 g) which initiated the precipitation of white microcrystals. These were filtered off, washed with ethanol and diethyl ether and air-dried (yield: 69%).

$[HgL'(Cl)]PF_6$. Addition of L′ (1.2 mmol) to a solution of $HgCl_2$ (1 mmol) in water (50 cm^3) caused the spontaneous precipitation of a colourless solid which dissolved again upon warming of the solution to 40 °C for ≈10 min. Upon addition of solid $NaPF_6$ (1.0 g) a white precipitate formed which was

Table 4 Atomic coordinates (× 10^4) for $[AgL'_2]PF_6$ **1**

Atom	*x*	*y*	*z*
Ag	0	5000	5000
N(1)	115(12)	2493(10)	5000
N(2)	−1921(7)	4099(8)	3846(6)
C(1)	−554(12)	2101(12)	4050(11)
C(2)	−1487(15)	2797(12)	3536(10)
C(3)	−3136(10)	4095(13)	4473(7)
C(4)	1515(14)	2028(14)	5000
C(5)	−2095(10)	4919(10)	2921(6)
P	0	5000	0
F(1)	199(6)	3905(5)	880(4)
F(2)	−1527(8)	4708(9)	0

Table 5 Atomic coordinates (× 10^4) for [AgL′(SCN)] **2**

Atom	*x*	*y*	*z*
Ag(1)	1007(1)	2500	2162(1)
S(1)	−1332(5)	2500	1855(2)
N(1)	−2805(16)	2500	2757(9)
N(2)	1950(12)	2500	3024(4)
N(3)	3008(8)	1264(7)	2144(4)
C(1)	−2150(18)	2500	2402(9)
C(2)	2761(14)	1503(12)	3080(5)
C(3)	3221(20)	932(13)	2669(6)
C(4)	4148(11)	1930(11)	1936(5)
C(5)	774(17)	2500	3388(6)
C(6)	2720(14)	347(10)	1756(5)
Ag(2)	−827(1)	2500	344(1)
S(11)	1516(5)	2500	655(2)
N(11)	2976(16)	2500	−281(8)
N(12)	−2800(10)	1302(8)	367(4)
N(13)	−1749(12)	2500	−528(5)
C(11)	2361(16)	2500	121(8)
C(12)	−2566(17)	1456(14)	−544(5)
C(13)	−3111(21)	985(16)	−127(6)
C(14)	−3928(14)	1961(12)	540(6)
C(15)	−636(18)	2500	−896(6)
C(16)	−2469(18)	364(11)	656(5)

filtered off, washed with ethanol and diethyl ether and air-dried (yield: 90%).

All new complexes gave satisfactory elemental analyses (C, H, N; Table 2).

X-Ray Crystallography.—Crystal data and details of intensity collection for complexes $[AgL'_2]PF_6$ and [AgL′(SCN)] are summarized in Table 3. Graphite-monochromated Mo-Kα radiation was used throughout. Crystal stabilities were monitored by recording three check reflections after every 400 measurements; no deterioration was observed, respectively. The two data sets were corrected for Lorentz and polarization effects, and were also corrected for absorption (ψ scans of seven reflections). The structures were solved by direct methods and Fourier-difference syntheses. Both structures were refined by least-squares techniques; the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. Neutral atom scattering factors were taken from ref. 10 and hydrogen-atom scattering factors from ref. 11. The positions of the methyl and methylene protons were calculated and included in the final refinement cycles with isotropic thermal parameters. Atom coordinates for $[AgL'_2]PF_6$ are given in Table 4, those for [AgL′(SCN)] in Table 5. Some special features of the crystal-structure determinations are discussed below.

Additional material available from the Cambridge Crystallographic Data Centre comprises the atom coordinates, thermal parameters and remaining bond lengths and angles.

$[AgL'_2]PF_6$. From the reflection conditions observed (00 *l*, $l = 2n$) three space groups ($P4_2$, $P4_2/m$, $P4_222$) are possible. Only the refinement in $P4_2/m$ converged smoothly and gave chemically reasonable bond distances. Both the cation and anion have crystallographically imposed site symmetry $2/m$ which is not compatible with the (λλλ) or (δδδ) configuration of the two co-ordinated 1,4,7-trimethyl-1,4,7-triazacyclononane ligands of the cation. Consequently, the C atoms of the methylene groups display physically meaningless, large, anisotropic thermal parameters due to disorder and the C–C bond distances are apparently too short (Table 1). Attempts to refine the structure by using a split-atom model failed. Introduction of constraints on C–C and C–N distances did not improve the refinement and were not used.

[AgL′(SCN)]. The neutral molecule [AgL′(SCN)] is bisected by a crystallographic mirror plane; atoms Ag(1), S(1), C(1), N(1), N(2) and C(5) lie on this plane. As described above for $[AgL'_2]PF_6$ this is not compatible with the (λλλ) or (δδδ) configuration of the nine-membered ligand ring co-ordinated to the silver ion. The consequences are as described above for $[AgL'_2]PF_6$.

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