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Acta Cryst. (1984). C**40**, 2014–2016

{2,16-Dimethyl-3,15,21-triaza-6,9,12-trithiabicyclo[15.3.1]henicosa-1(21),2,15,17,19-pentaene}silver(I) Tetraphenylborate, $[Ag(C_{17}H_{25}N_3S_3)][B(C_6H_5)_4]$

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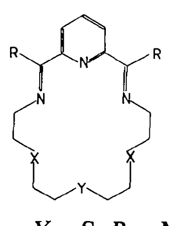
(*Received* 4 *June* 1984; *accepted* 2 *July* 1984)

Abstract. $M_r = 794{\cdot}7$, triclinic, $P\bar{1}$, $a = 13{\cdot}863\,(9)$, $b = 10{\cdot}965\,(11)$, $c = 14{\cdot}990\,(12)$ Å, $\alpha = 109{\cdot}0\,(1)$, $\beta = 99{\cdot}2\,(1)$, $\gamma = 65{\cdot}0\,(1)°$, $U = 1957{\cdot}1$ Å^3, $Z = 2$, D_m(flotation) = 1·35 (2), $D_x = 1{\cdot}35$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 6{\cdot}90$ cm^{-1}, $F(000) = 824$, room temperature (space group established from the successful structure determination). 3966 independent reflections; $R = 0{\cdot}063$. The structure consists of discrete $[AgL^1]$ cations (L^1 represents the macrocycle) and $[BPh_4]$ anions. The Ag atoms are six-coordinate, being bonded to three N atoms [2·613 (9), 2·422 (9), 2·399 (7) Å] and three S atoms [2·670 (3), 2·655 (3), 2·949 (4) Å]. The geometry of the coordination sphere is irregular.

Introduction. We are investigating the relationship between macrocycle conformation and 'hole' size and the effect upon metal complexation. 18-membered macrocycles of type L are particularly interesting as in a planar conformation they produce a hole size only suitable for the larger metal ions, such as Pb^{2+}, Ca^{2+}, Sr^{2+}.



L^1 $X = Y = S, R = Me$
L^2 $X = Y = O, R = H$
L^3 $X = S, Y = O, R = Me$

Several structures have been determined for macrocycle complexes of L, *viz* $[CaL^2(NCS)_2]$, $[SrL^2(NCS)_2]$ (Fenton, Cook, Nowell & Walker, 1978), $[PbL^2(NCS)_2]$ (Nowell, 1979), $[PbL^3(NCS)_2]$ (Richards, 1978) and $[PbL^3(OH_2)(ClO_4)]$ (Silong, 1983). In these structures the metal atom is 8- or 9-coordinate being bonded to the six donor atoms of the macrocycle and two (or three) anionic ligands. In $[CaL^2(NCS)_2]$, the Ca atom occupies a distorted hexagonal bipyramid with the macrocycle providing the planar girdle and the two thiocyanates in axial positions. This suggests that the ion fits satisfactorily into the planar macrocycle 'hole'. With the larger Pb and Sr atoms, the macrocycle is less planar.

The title compound $[AgL^1][BPh_4]$ is a particularly interesting member of this series because it is certain to have a different structure. The tetraphenylborate anion is non-coordinating and also the silver ion is smaller than those atoms in the analogous macrocycle complexes and therefore the conformation of L^1 must be radically different from that of L^2 or L^3 in the complexes if it is to be 6-coordinate and accommodate the silver ion.

Experimental. The title compound (I) was prepared by adding a solution of 2,6-diacetylpyridine (3·26 g, 0·02 mol) in methanol (50 cm^3) to a methanolic solution of silver nitrate (3·39 g, 0·02 mol in 450 cm^3). The solution was rapidly stirred and warmed. Then followed the dropwise addition of a solution of 1,11-diamino-3,6,9-trithiaundecane (prepared following Drew, Rice & Richards, 1980) (4·81 g, 0·02 mol) in methanol (50 cm^3). The reaction mixture was allowed to reflux for 20 h. Sodium perchlorate (8 g) in ethanol (50 cm^3) was added and the reaction mixture allowed to stand for 1 d. A yellow crystalline product $[AgL^1]$-$[ClO_4]$ was obtained in 74% yield, which then reacted in (1:1) ratio with $NaBPh_4$ in methanol to give $[AgL^1][BPh_4]$ (I) in 77% yield. (I) was recrystallized from an acetonitrile/methanol mixture.

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Crystal 0·3 × 0·3 × 0·3 mm, mounted on a Stoe STADI2 diffractometer to rotate around the c axis. Cell dimensions by measurement of high-angle axial reflections, intensity data collected *via* variable-width ω scan. 20 s background counts, step-scan rate 0·033° s^{-1}, width (1·5 + sin $\mu/\tan\theta$) mm. $2\theta_{max} = 50°$ ($\pm h$, $\pm k$, l). No absorption and extinction corrections. Standard reflections measured every 2θ measurements for each layer, no significant change in intensity observed at end of data collection. 6415 independent reflections measured, 3966 with $I > 3\sigma(I)$ used in subsequent calculations. Structure determination by Patterson map, all non-hydrogen atoms from Fourier maps. The H atoms bonded to C were positioned in trigonal or tetrahedral sites, 0·95 Å from the respective bonded atoms. H atoms belonging to the same phenyl ring were given equivalent thermal parameters. H atoms on the two methyl C atoms could not be located. Anisotropic refinement on F of non-hydrogen atoms. Final R = 0·063 (R_w = 0·067). Final shifts ≤0·2σ. Calculations performed using *SHELX*76 (Sheldrick, 1976) at the University of Manchester Regional Computing Centre. Scattering factors from *International Tables for X-ray Crystallography* (1974). Weighting scheme chosen to give similar values of $w\Delta^2$ over ranges of sin θ/λ and F_o; $w = 1/[\sigma^2(F) + 0{\cdot}002F^2]$ where $\sigma(F)$ was taken from counting statistics. The difference Fourier maps showed no significant peaks. Atomic coordinates for (I) are given in Table 1 and molecular dimensions in Table 2.*

Table 1. *Atomic coordinates* (× 10^4) *and* $\bar{U}$ *values* (× 10^3) *with e.s.d.'s in parentheses*

$$\bar{U} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$\bar{U}$(Å^2)
Ag	704 (1)	621 (1)	2385·3 (4)	89 (1)
S(18)	1216 (3)	2182 (3)	4010 (2)	97 (4)
S(21)	2185 (2)	−1460 (3)	2986 (2)	105 (4)
S(15)	−725 (2)	883 (3)	3760 (2)	102 (4)
N(1)	2512 (6)	171 (9)	1755 (6)	100 (11)
C(2)	2464 (7)	869 (11)	1233 (9)	122 (16)
C(3)	3362 (18)	1186 (24)	1076 (16)	225 (9)
C(4)	1465 (7)	1379 (10)	694 (7)	89 (13)
N(5)	623 (5)	1329 (7)	995 (5)	76 (10)
C(6)	−312 (7)	1775 (9)	538 (7)	78 (12)
C(7)	−430 (9)	2259 (11)	−255 (7)	111 (15)
C(8)	428 (11)	2354 (13)	−537 (9)	144 (20)
C(9)	1362 (9)	1931 (11)	−80 (8)	130 (17)
C(10)	−1242 (7)	1752 (9)	947 (7)	74 (12)
C(11)	−2320 (8)	2291 (12)	441 (9)	107 (16)
N(12)	−1059 (6)	1348 (8)	1697 (5)	82 (11)
C(13)	−1912 (8)	1338 (13)	2133 (7)	106 (16)
C(14)	−1860 (8)	1996 (12)	3222 (8)	119 (16)
C(16)	−480 (10)	2090 (12)	4822 (7)	106 (16)
C(17)	12 (10)	3034 (11)	4704 (8)	109 (17)
C(19)	2140 (10)	885 (13)	4591 (9)	120 (20)
C(20)	2163 (10)	−567 (13)	4260 (8)	125 (19)
C(22)	3420 (8)	−1635 (13)	2571 (10)	135 (18)
C(23)	3405 (7)	357 (12)	2377 (9)	124 (17)
B	2907 (9)	3141 (11)	7635 (8)	77 (14)
C(31)	3267 (8)	3916 (9)	7045 (7)	84 (13)
C(32)	2897 (10)	3878 (10)	6103 (8)	103 (16)
C(33)	3251 (11)	4339 (11)	5510 (9)	136 (19)
C(34)	3992 (12)	4913 (13)	5842 (12)	173 (23)
C(35)	4353 (10)	5027 (13)	6758 (13)	165 (23)
C(36)	3992 (8)	4540 (10)	7376 (9)	105 (15)
C(41)	3605 (7)	1439 (9)	7257 (7)	81 (12)
C(42)	4118 (7)	742 (10)	6376 (7)	83 (13)
C(43)	4629 (8)	−710 (11)	6051 (8)	94 (15)
C(44)	4665 (9)	−1512 (12)	6597 (10)	105 (17)
C(45)	4183 (8)	−852 (11)	7480 (9)	123 (17)
C(46)	3676 (8)	551 (10)	7793 (8)	102 (14)
C(51)	1628 (7)	3520 (9)	7440 (6)	72 (12)
C(52)	1163 (7)	2565 (9)	7265 (6)	78 (12)
C(53)	68 (7)	2941 (10)	7187 (6)	83 (13)
C(54)	−618 (8)	4311 (11)	7288 (6)	87 (14)
C(55)	−180 (8)	5281 (11)	7445 (7)	92 (14)
C(56)	900 (8)	4906 (10)	7523 (7)	84 (13)
C(61)	3130 (8)	3646 (9)	8813 (7)	82 (13)
C(62)	2324 (8)	4287 (9)	9483 (7)	84 (13)
C(63)	2534 (10)	4671 (11)	10479 (7)	106 (16)
C(64)	3573 (11)	4408 (13)	10820 (9)	118 (21)
C(65)	4364 (10)	3811 (14)	10171 (9)	104 (20)
C(66)	4152 (9)	3411 (13)	9180 (9)	105 (17)

Table 2. *Dimensions in the coordination sphere* (Å *and* deg)

Ag—S(18)	2·670 (3)	Ag—N(1)	2·613 (9)
Ag—S(21)	2·655 (3)	Ag—N(5)	2·422 (9)
Ag—S(15)	2·949 (4)	Ag—N(12)	2·399 (7)
S(18)—Ag—S(21)	82·41 (9)	S(15)—Ag—N(5)	139·89 (17)
S(18)—Ag—S(15)	75·93 (10)	N(1)—Ag—N(5)	63·04 (26)
S(21)—Ag—S(15)	87·39 (10)	S(18)—Ag—N(12)	121·98 (17)
S(18)—Ag—N(1)	87·13 (19)	S(21)—Ag—N(12)	142·21 (25)
S(21)—Ag—N(1)	73·52 (23)	S(15)—Ag—N(12)	73·39 (23)
S(15)—Ag—N(1)	156·07 (20)	N(1)—Ag—N(12)	130·48 (30)
S(18)—Ag—N(5)	116·02 (20)	N(5)—Ag—N(12)	68·03 (29)
S(21)—Ag—N(5)	130·64 (16)		

Discussion. The unit cell contains discrete [AgL^1] cations and [BPh_4] anions. In the cation (Fig. 1), the Ag atom is bonded to all six donor atoms in the macrocycle, *viz* three N atoms [Ag—N(1) 2·613 (9), Ag—N(5) 2·422 (9), Ag—N(12) 2·399 (7) Å] and three S atoms [Ag—S(18) 2·670 (3), Ag—S(21) 2·655 (3), Ag—S(15) 2·949 (4) Å] of the macrocycle.

The silver coordination sphere, as is apparent from the bond lengths and angles, is highly irregular, being neither octahedral nor trigonal prismatic. The trimethine group makes up an approximately planar

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and remaining bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39616 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

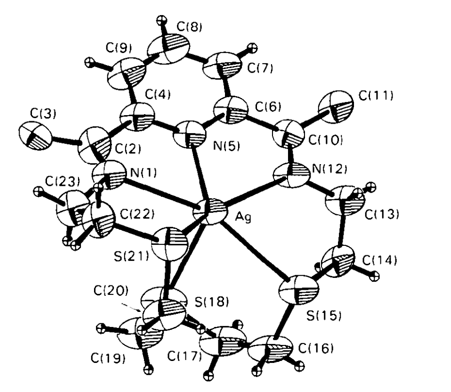

Fig. 1. The structure of the [AgL^1] cation. Ellipsoids are shown at 40% probability.

AgN_3 group but the three S atoms S(15), S(18), S(21) deviate from this plane by distances of 0·52 (1), 2·32 (1), −1·05 (1) Å respectively. Although S(18) is displaced 2·32 (1) Å from the AgN_3 plane, it is not in the axial position as the three S(18)—Ag—N angles range from 87·1 (2) to 122·0 (2)°.

In the aforementioned structures of L^2 and L^3 macrocycles with Pb, Ca and Sr, the macrocycles are closer to planarity. A rough measure of this non-planarity is the deviations of the three donor atoms X,Y,X (X,Y = O or S) from the MN_3 plane, as in these structures the maximum deviations are *ca* 1·5 Å compared to 2·32 (1) Å for S(18) in the present structure.

The different macrocycle conformation in the present cation is caused by a mismatch between the small size of the silver ion and the larger macrocycle cavity, though it is possible that the non-coordinating nature of the anion may be a contributory factor. With thiocyanate (say) a more planar geometry of the macrocycle may have been observed. However, attempts to prepare compounds with coordinating unidentate anions were not successful. Because of the strong affinity of the silver(I) ions towards these anions, the simple silver(I) salts were precipitated.

Another feature of the structure which supports the suggestion of a mismatch between metal and 'hole' size is the variation in bond lengths between the metal and the donor atoms. In particular we note that Ag(1)—N(1) is 0·20 Å longer than the equivalent Ag(1)—N(12) bond and that Ag—S(15) is *ca* 0·30 Å longer than the other two Ag—S bonds. N(1) and S(15) are on opposite sides of the molecule and clearly these increases are caused by the need to alleviate strain. However, there were no unexpected torsion angles in the macrocycle, the most strained being S(18)—C(19)—C(20)—S(21) at 46·0°.

There are no contacts between cation and anion of less than 3·7 Å. The geometry of the tetraphenylborate anion is as expected.

We thank SERC for a grant for the diffractometer and A. W. Johans for his help with the crystallographic investigations. SS thanks the Agricultural University of Malaysia for study leave.

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Acta Cryst. (1984). C**40**, 2016–2019

The Structures of α-Ketoglutaric Acid (I),* $C_5H_6O_5$, Sodium Hydrogen α-Ketoglutarate (II), $Na^+.C_5H_5O_5^-$, and Potassium Hydrogen α-Ketoglutarate (III), $K^+.C_5H_5O_5^-$

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(*Received* 23 *February* 1984; *accepted* 2 *July* 1984)

Abstract. (I) M_r = 146·1, monoclinic, $P2_1/c$, a = 16·71 (2), b = 6·375 (4), c = 5·525 (6) Å, β = 94·73 (7)°, V = 586·6 Å^3, T = 302 (2) K, Z = 4, D_m = 1·64, D_x = 1·65 Mg m^{-3}, $F(000)$ = 304, μ(Mo $K\alpha$, λ = 0·71069 Å) = 0·16 mm^{-1}, final R = 0·051 and R_w = 0·052 for 1338 non-zero reflexions. (II) M_r = 168·1, orthorhombic, $Pbca$, a = 6·113 (5), b = 5·859 (7), c = 34·76 (4) Å, V = 1245 Å^3, T = 304 (2) K, Z = 8, D_m = 1·79, D_x = 1·79 Mg m^{-3}, $F(000)$ = 688, μ(Mo $K\alpha$) = 0·23 mm^{-1}, final R = 0·040 and R_w = 0·047 for 1594 non-zero reflexions. (III) M_r = 184·2, monoclinic, $P2_1/c$, a = 6·517 (4), b = 17·816 (9), c = 8·050 (4) Å, β = 131·79 (4)°, V = 696·9 Å^3, T = 298 (2) K, Z = 4, D_m = 1·74, D_x = 1·76 Mg m^{-3}, $F(000)$ = 376, μ(Mo $K\alpha$) = 0·73 mm^{-1}, final R = 0·033 and R_w = 0·036 for 1869

* 2-Oxoglutaric acid.

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