Discussion. Final positional parameters for the non-H atoms are listed in Table 1, and bond lengths and angles in Table 2.* A *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule is given in Fig. 1 and the Newman projection along the C(9)—C(1′) bond in Fig. 2. A least-squares plane through the acridinium atoms shows that the maximum distance of one of its constituent atoms from this plane is 0·103 Å. The phenyl ring is planar to within 0·007 Å. The angle between the two planes is 82°. The O atoms of the crown ether alternate about 0·10 Å above and below their mean plane; the N atom lies 1·24 Å below this plane. For the mean cavity radius, as defined by Mathieu, Metz, Moras & Weiss (1978), a value of 1·08 Å was obtained. The distance from the Na ion to the centre of gravity of the hetero atoms in the crown ether is 0·87 Å, the angle N(1″)–centre of gravity–Na is 87°. The Na ion is coordinated by the four O atoms of the crown ether and by the N atom of the thiocyanate ion.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52630 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1990). C**46**, 1089–1091

Crystal Studies of Acridinium Dyes. XVI.* Another Modification of 10-Methyl-9-[4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenyl]acridinium Silver Diperchlorate Acetonitrile Solvate

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Abstract. $C_{30}H_{35}N_2O_4^+.Ag^+.2ClO_4^-.CH_3CN$, M_r = 835·5, monoclinic, $P2_1/a$, a = 11·805 (5), b = 26·770 (18), c = 11·475 (5) Å, β = 100·37 (4)°, V = 3567 (4) Å^3, Z = 4, D_x = 1·56 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 7·7 cm^{-1}, F(000) = 1712, room temperature. Final R = 0·074 for 2873 observed reflections. The angle between the planes of the acridinium and the phenyl groups is 61°. The mean cavity radius of the crown ether is 1·15 Å. The Ag atom is coordinated by the five hetero atoms of the crown ether and the N atom of the acetonitrile solvent.

Introduction. This is the sixteenth paper in a series of acridinium dyes. In this case the phenyl ring is substituted with an aza-15-crown-5 group, which has formed a complex with silver perchlorate. This is the same compound as in the seventh paper of this series (Kronenberg, Reiss, Goubitz & Heijdenrijk, 1989) but the crystals contain a different solvent molecule, acetonitrile instead of dichloromethane.

Experimental. A red plate-shaped crystal (dimensions 0·15 × 0·30 × 0·40 mm approximately) was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation and ω–2θ scans. A total of 6269 unique reflections was measured within the range $-13 \le h \le 13$, $0 \le k \le 30$, $0 \le l \le 13$. Of these, 2873 were above the significance level of $2·5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0·59 Å^{-1}. Three standard

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* Part XV, preceding paper.

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters*

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Ag	0·19843 (8)	0·09826 (4)	0·24932 (8)	0·0721 (6)
Cl(1)	0·2006 (3)	0·0090 (2)	0·7901 (3)	0·088 (2)
Cl(2)	0·2236 (4)	0·3334 (1)	0·6257 (4)	0·093 (3)
C(1)	−0·252 (1)	0·2945 (4)	−0·003 (1)	0·066 (8)
C(2)	−0·280 (1)	0·3388 (5)	−0·059 (1)	0·09 (1)
C(3)	−0·370 (1)	0·3413 (5)	−0·153 (1)	0·09 (1)
C(4)	−0·432 (1)	0·3009 (6)	−0·197 (1)	0·09 (1)
C(5)	−0·533 (1)	0·1279 (6)	−0·150 (1)	0·082 (9)
C(6)	−0·508 (1)	0·0825 (6)	−0·090 (2)	0·10 (1)
C(7)	−0·413 (1)	0·0765 (6)	−0·002 (2)	0·10 (1)
C(8)	−0·341 (1)	0·1158 (5)	0·033 (1)	0·080 (9)
C(9)	−0·2907 (9)	0·2041 (4)	0·013 (1)	0·058 (7)
C(11)	−0·571 (1)	0·2152 (7)	−0·278 (2)	0·11 (1)
N(10)	−0·4761 (9)	0·2132 (4)	−0·1738 (9)	0·076 (7)
O(1)	0·235 (1)	0·0193 (5)	0·911 (1)	0·13 (1)
O(2)	0·101 (1)	0·0351 (7)	0·741 (2)	0·18 (1)
O(3)	0·281 (2)	0·024 (1)	0·734 (2)	0·31 (3)
O(4)	0·177 (3)	−0·0398 (7)	0·765 (2)	0·32 (3)
O(5)	0·314 (2)	0·336 (1)	0·576 (2)	0·31 (3)
O(6)	0·183 (2)	0·2858 (6)	0·629 (2)	0·21 (2)
O(7)	0·265 (2)	0·337 (1)	0·747 (2)	0·26 (3)
O(8)	0·146 (2)	0·3687 (7)	0·621 (2)	0·22 (2)
C(2″)	0·199 (1)	0·2122 (5)	0·385 (1)	0·09 (1)
C(3″)	0·317 (1)	0·1928 (6)	0·399 (1)	0·10 (1)
C(5″)	0·453 (2)	0·1571 (7)	0·286 (3)	0·16 (2)
C(6″)	0·478 (1)	0·1135 (9)	0·291 (3)	0·16 (2)
C(8″)	0·433 (2)	0·030 (1)	0·259 (5)	0·34 (5)
C(9″)	0·374 (2)	−0·0049 (9)	0·282 (2)	0·16 (2)
C(11″)	0·244 (2)	−0·0068 (6)	0·418 (2)	0·10 (1)
C(12″)	0·136 (1)	0·0176 (5)	0·437 (1)	0·09 (1)
C(14″)	0·057 (1)	0·0968 (5)	0·473 (1)	0·081 (9)
C(15″)	0·093 (1)	0·1505 (5)	0·482 (1)	0·078 (9)
N(1″)	0·108 (1)	0·1725 (4)	0·3662 (9)	0·074 (7)
O(4″)	0·3329 (7)	0·1708 (4)	0·2951 (9)	0·089 (6)
O(7″)	0·407 (1)	0·0787 (5)	0·233 (2)	0·15 (1)
O(10″)	0·260 (1)	0·0089 (4)	0·304 (1)	0·104 (8)
O(13″)	0·1560 (7)	0·0702 (3)	0·4446 (7)	0·069 (5)
C(1′)	−0·188 (1)	0·1987 (5)	0·122 (1)	0·070 (8)
C(2′)	−0·078 (1)	0·2081 (5)	0·087 (1)	0·067 (8)
C(3′)	0·017 (1)	0·1986 (5)	0·174 (1)	0·071 (8)
C(4′)	0·007 (1)	0·1827 (4)	0·289 (1)	0·061 (7)
C(5′)	−0·105 (1)	0·1755 (4)	0·311 (1)	0·065 (8)
C(6′)	−0·198 (1)	0·1826 (5)	0·224 (1)	0·064 (7)
C(4*a*)	−0·412 (1)	0·2542 (5)	−0·140 (1)	0·071 (8)
C(8*a*)	−0·363 (1)	0·1624 (5)	−0·023 (1)	0·066 (8)
C(9*a*)	−0·316 (1)	0·2507 (5)	−0·044 (1)	0·068 (8)
C(10*a*)	−0·456 (1)	0·1684 (5)	−0·115 (1)	0·069 (8)
C(1*s*)	−0·091 (1)	0·0623 (5)	−0·083 (1)	0·086 (9)
C(2*s*)	−0·003 (1)	0·0725 (5)	0·013 (1)	0·067 (8)
N(*s*)	0·0664 (9)	0·0832 (4)	0·0909 (9)	0·072 (7)

Table 2. *Bond lengths* (Å) *and angles* (°)

Ag—N(1″)	2·72 (1)	N(10)—C(4*a*)	1·35 (2)
Ag—O(4″)	2·503 (9)	N(10)—C(10*a*)	1·38 (2)
Ag—O(7″)	2·56 (1)	C(2″)—C(3″)	1·47 (2)
Ag—O(10″)	2·55 (1)	C(2″)—N(1″)	1·49 (2)
Ag—O(13″)	2·499 (8)	C(3″)—O(4″)	1·37 (2)
Ag—N(*s*)	2·21 (1)	C(5″)—C(6″)	1·20 (3)
Cl(1)—O(1)	1·40 (1)	C(5″)—O(4″)	1·49 (2)
Cl(1)—O(2)	1·40 (2)	C(6″)—O(7″)	1·34 (3)
Cl(1)—O(3)	1·30 (2)	C(8″)—C(9″)	1·23 (4)
Cl(1)—O(4)	1·36 (2)	C(8″)—O(7″)	1·35 (3)
Cl(2)—O(5)	1·30 (3)	C(9″)—O(10″)	1·46 (3)
Cl(2)—O(6)	1·37 (2)	C(11″)—C(12″)	1·47 (2)
Cl(2)—O(7)	1·39 (2)	C(11″)—O(10″)	1·42 (2)
Cl(2)—O(8)	1·31 (2)	C(12″)—O(13″)	1·43 (2)
C(1)—C(2)	1·36 (2)	C(14″)—C(15″)	1·50 (2)
C(1)—C(9*a*)	1·43 (2)	C(14″)—O(13″)	1·46 (2)
C(2)—C(3)	1·37 (2)	C(15″)—N(1″)	1·50 (2)
C(3)—C(4)	1·35 (2)	N(1″)—C(4′)	1·38 (2)
C(4)—C(4*a*)	1·41 (2)	C(1′)—C(2′)	1·40 (2)
C(5)—C(6)	1·40 (2)	C(1′)—C(6′)	1·38 (2)
C(5)—C(10*a*)	1·42 (2)	C(2′)—C(3′)	1·39 (2)
C(6)—C(7)	1·39 (2)	C(3′)—C(4′)	1·42 (2)
C(7)—C(8)	1·36 (2)	C(4′)—C(5′)	1·40 (2)
C(8)—C(8*a*)	1·40 (2)	C(5′)—C(6′)	1·36 (2)
C(9)—C(1′)	1·51 (2)	C(4*a*)—C(9*a*)	1·44 (2)
C(9)—C(8*a*)	1·42 (2)	C(8*a*)—C(10*a*)	1·39 (2)
C(9)—C(9*a*)	1·42 (2)	C(1*s*)—C(2*s*)	1·40 (2)
C(11)—N(10)	1·49 (2)	C(2*s*)—N(*s*)	1·14 (1)
N(1″)—Ag—O(4″)	67·5 (3)	C(12″)—C(11″)—O(10″)	105 (1)
N(1″)—Ag—O(7″)	130·7 (4)	C(11″)—C(12″)—O(13″)	108 (1)
N(1″)—Ag—O(10″)	133·2 (4)	C(15″)—C(14″)—O(13″)	105 (1)
N(1″)—Ag—O(13″)	67·6 (3)	C(14″)—C(15″)—N(1″)	113 (1)
N(1″)—Ag—N(*s*)	105·0 (4)	Ag—N(1″)—C(2″)	105·0 (8)
O(4″)—Ag—O(7″)	65·9 (4)	Ag—N(1″)—C(15″)	105·9 (7)
O(4″)—Ag—O(10″)	122·4 (3)	Ag—N(1″)—C(4′)	101·4 (7)
O(4″)—Ag—O(13″)	105·5 (3)	C(2″)—N(1″)—C(15″)	111 (1)
O(4″)—Ag—N(*s*)	129·9 (4)	C(2″)—N(1″)—C(4′)	118 (1)
O(7″)—Ag—O(10″)	65·8 (4)	C(15″)—N(1″)—C(4″)	114 (1)
O(7″)—Ag—O(13″)	110·7 (4)	Ag—O(4″)—C(3″)	109·7 (8)
O(7″)—Ag—N(*s*)	116·7 (5)	Ag—O(4″)—C(5″)	111·8 (9)
O(10″)—Ag—O(13″)	65·8 (3)	C(3″)—O(4″)—C(5″)	116 (1)
O(10″)—Ag—N(*s*)	99·2 (4)	Ag—O(7″)—C(6″)	110 (1)
O(13″)—Ag—N(*s*)	117·2 (3)	Ag—O(7″)—C(8″)	111 (2)
O(1)—Cl(1)—O(2)	112 (1)	C(6″)—O(7″)—C(8″)	117 (2)
O(1)—Cl(1)—O(3)	109 (1)	Ag—O(10″)—C(9″)	115 (1)
O(1)—Cl(1)—O(4)	114 (1)	Ag—O(10″)—C(11″)	115·3 (9)
O(2)—Cl(1)—O(3)	107 (1)	C(9″)—O(10″)—C(11″)	111 (1)
O(2)—Cl(1)—O(4)	106 (1)	Ag—O(13″)—C(12″)	107·2 (8)
O(3)—Cl(1)—O(4)	109 (2)	Ag—O(13″)—C(14″)	110·5 (7)
O(5)—Cl(2)—O(6)	113 (2)	C(12″)—O(13″)—C(14″)	112 (1)
O(5)—Cl(2)—O(7)	105 (1)	C(9)—C(1′)—C(2′)	119 (1)
O(5)—Cl(2)—O(8)	124 (2)	C(9)—C(1′)—C(6′)	122 (1)
O(6)—Cl(2)—O(7)	96 (1)	C(2′)—C(1′)—C(6′)	119 (1)
O(6)—Cl(2)—O(8)	115 (1)	C(1′)—C(2′)—C(3′)	119 (1)
O(7)—Cl(2)—O(8)	96 (2)	C(2′)—C(3′)—C(4′)	122 (1)
C(2)—C(1)—C(9*a*)	119 (1)	N(1″)—C(4′)—C(3′)	117 (1)
C(1)—C(2)—C(3)	120 (1)	N(1″)—C(4′)—C(5′)	127 (1)
C(2)—C(3)—C(4)	123 (1)	C(3′)—C(4′)—C(5′)	117 (1)
C(3)—C(4)—C(4*a*)	120 (1)	C(4′)—C(5′)—C(6′)	121 (1)
C(6)—C(5)—C(10*a*)	117 (1)	C(1′)—C(6′)—C(5′)	122 (1)
C(5)—C(6)—C(7)	122 (1)	C(4)—C(4*a*)—N(10)	123 (1)
C(6)—C(7)—C(8)	120 (1)	C(4)—C(4*a*)—C(9*a*)	117 (1)
C(7)—C(8)—C(8*a*)	120 (1)	N(10)—C(4*a*)—C(9*a*)	120 (1)
C(1′)—C(9)—C(8*a*)	120 (1)	C(8)—C(8*a*)—C(9)	121 (1)
C(1′)—C(9)—C(9*a*)	120 (1)	C(8)—C(8*a*)—C(10*a*)	120 (1)
C(8*a*)—C(9)—C(9*a*)	120 (1)	C(9)—C(8*a*)—C(10*a*)	119 (1)
C(11)—N(10)—C(4*a*)	120 (1)	C(1)—C(9*a*)—C(9)	121 (1)
C(11)—N(10)—C(10*a*)	118 (1)	C(1)—C(9*a*)—C(4*a*)	120 (1)
C(4*a*)—N(10)—C(10*a*)	122 (1)	C(9)—C(9*a*)—C(4*a*)	119 (1)
C(3″)—C(2″)—N(1″)	114 (1)	C(5)—C(10*a*)—N(10)	119 (1)
C(2″)—C(3″)—O(4″)	109 (1)	C(5)—C(10*a*)—C(8*a*)	120 (1)
C(6″)—C(5″)—O(4″)	117 (2)	N(10)—C(10*a*)—C(8*a*)	121 (1)
C(5″)—C(6″)—O(7″)	122 (2)	C(1*s*)—C(2*s*)—N(*s*)	176 (1)
C(9″)—C(8″)—O(7″)	132 (3)	Ag—N(*s*)—C(2*s*)	175 (1)
C(8″)—C(9″)—O(10″)	115 (2)		

reflections (140, 002, $\bar{2}22$) were measured hourly; a 5% decrease was measured during the 70 h collection time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $20 < 2\theta < 30°$. Corrections for Lorentz and polarization effects and for the variation in the standard intensities were applied. The structure was solved by the Patterson superposition technique using *SAPI* (Yao Jia-xing *et al.*, 1985). The positions of the H atoms, were calculated and kept fixed during refinement with $U = 0·06$ Å^2. Block-diagonal least-squares refinement on F, anisotropic for the non-H atoms, converged to $R = 0·074$, $wR = 0·118$, $(\Delta/\sigma)_{\max} = 0·59$. The two perchlorate ions show considerable thermal anisotropy. A weighting scheme $w = (4·04 + F_o + 0·030F_o^2)^{-1}$ was used. An empirical absorption correction was applied, with corrections in the range 0·66–1·30 (*DIFABS*; Walker & Stuart, 1983). A final difference synthesis revealed residual electron density between −0·4 and 0·9 e Å^{-3}. Scattering factors were taken from Cromer & Mann (1968) and from *International Tables for X-ray Crystallography* (1974). Anomalous dispersion for Ag and Cl was corrected for. All calculations were performed with *XRAY76* (Stewart *et al.*, 1976), unless stated otherwise.

Discussion. Final positional parameters for the non-H atoms are listed in Table 1, bond lengths and angles in Table 2.* A *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule is given in Fig. 1 and the Newman projection along the C(9)—C(1′) bond in Fig. 2. A least-squares plane through the acridinium atoms shows that the maximum distance of a constituent atom from this plane is 0·096 Å. The phenyl ring is planar to within 0·016 Å. The twist angle between the two planes is 61°. The O atoms of the crown ether alternate about 0·12 Å above and below their mean plane; the N atom lies 1·1 Å below this plane. For the mean cavity radius, as defined by Mathieu, Metz, Moras & Weiss (1978), a value of 1·15 Å was obtained. The distance from the Ag ion to the centre of gravity of the hetero atoms in the crown ether is 1·02 Å and the angle N(1″)–centre of gravity–Ag is 82°. The Ag ion is coordinated by the five hetero atoms of the crown ether and the N atom of the acetonitrile solvent. There are two main differences between this modification and the one described in the paper VII of this series (Kronenberg *et al.*, 1989). The first difference is in the twist angle (74° in VII) and the second is in the coordination of the Ag ion. In both modifications the Ag is bonded to the five hetero atoms of the crown ether, in VII the sixth bond is to a perchlorate ion and not, as in this case, to a solvent molecule.

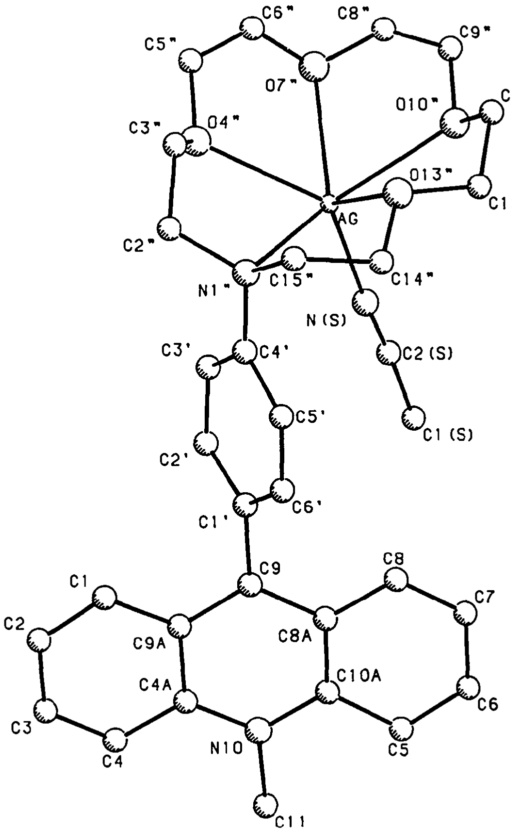

Fig. 1. Structure of $[C_{30}H_{35}N_2O_4.Ag.CH_3CN]^{2+}$ showing the numbering scheme.

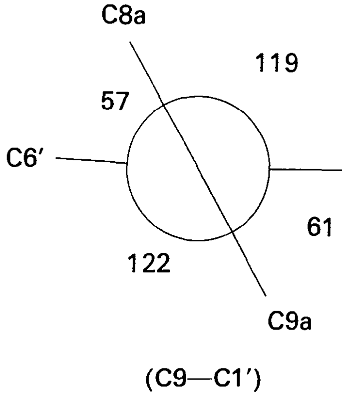

Fig. 2. The Newman projection along the C(9)—C(1′) bond.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52631 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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