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Silver Ion Complexation by a Calix[4]arene *bis*(Crown Ether): Ambivalence Towards Ether and Polyhapto Coordinations

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The synthesis and crystal structure of the Ag^+ ion complex of calix[4]arene *bis*(crown-6), BC6, are reported. $Ag_2BC6(NO_3)_2(H_2O)_{1+x}\cdot(DMF)_{0.5}$, with x refined to 0.87 (1), crystallizes in the monoclinic space group C2, $a = 33.598(2)$, $b = 11.4711(3)$, $c = 13.7755(7)$ Å, $\beta = 104.585(2)°$, $V = 5138(2)$ Å^3, $Z = 4$. Refinement led to a final conventional R_1 value of 0.064 for 10401 reflections and 660 parameters. The two silver ions, located in each site of the ditopic calixcrown, are disordered over two positions each, one of them corresponding mainly to a bonding to ether oxygen atoms and the other to a polyhapto bonding with calixarene phenyl rings. Three metal ion positions are located near the crown ether extremity, whereas one of the polyhapto-bonded ions is displaced towards the calixarene cavity. This result provides an illustration of the ambivalent character of silver ions, which may accomodate either ethereal or π-basic coordination sites and of the ability of 1,3-*alternate* calix[4]crowns to provide both types of environment. Extraction and complexation studies of Ag^+ in methanol and acetonitrile by BC6 and related calix[4]arene *bis*(crowns) are also presented. The results show that the 1:1 species only, whose stabilization is purely enthalpic in origin, is present in solution.

Keywords: Calixarene, calixcrown, silver complex, extraction, stability constants, complexation thermodynamics

INTRODUCTION

Calix[4]arene *bis*(crown ethers), in which the calixarene is blocked in the 1,3-*alternate* conformation, are ditopic ligands with a high potential for alkali metal ion complexation and particularly, in the case of the crown-6 derivative, a remarkable Cs^+/Na^+ selectivity [1–3]. This particular affinity for the soft caesium cation is thought to be partly the result of interactions with the π systems of the two phenyl rings nearer to the cation, as already suggested for *mono*(crown ether) derivatives fixed in the 1,3-*alternate* conformation [4,5]. We have determined various crystal structures of calix[4]arene *bis*(crown ethers) and their alkali-metal ion complexes [6]: the caesium complexes structures

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confirm the possibility of π-bonding, along with coordination with the six ether oxygen atoms, whereas in the sodium complex, in which the complexed species is in fact $Na(H_2O)^+$, the cation interacts with three phenolic oxygen atoms only and is located in the ether loop end, well outside the calixarene cavity [7]. On the other hand, apart from more usual complexes, silver ions are known to readily form complexes with electron-rich systems such as alkenes and aromatic rings [8]: such complexes have been characterized in the case of cyclophanes (π-prismands, deltaphane), stilbene or tubelike hydrocarbons [9–16] and the crystal structures of some of them determined, which evidence a π-bonding of silver with three to six carbon atoms. Some examples of phenyl-bonded silver ions have also been given in the domain of calixarene chemistry [17–22]. In particular, Ag^+ has been shown to be included in the π-basic cavity of calix[4]arenes in *cone* or partial *cone* conformations, and not in the site defined by the lower rim oxygen atoms [18, 19]. So, it appeared interesting, since calix[4]arene *bis*(crown-6) was able to provide both a coordination site formed by two roughly parallel phenyl rings and an array of six ether oxygen atoms, to investigate its complexing properties towards Ag^+ ions. The crystal structure of the complex obtained is reported here. The binding of silver cations in solution by **BC6** and three related calix [4]arene *bis*(crowns) (Fig. 1) has also been established by extraction experiments from water into dichloromethane and by determination of the thermodynamic parameters of complexation in methanol and acetonitrile.

RESULTS AND DISCUSSION

Crystal Structure

Notwithstanding a 2:1 metal/ligand ratio usual for this ditopic ligand when an excess of metal salt is used, the silver ions appear to be highly

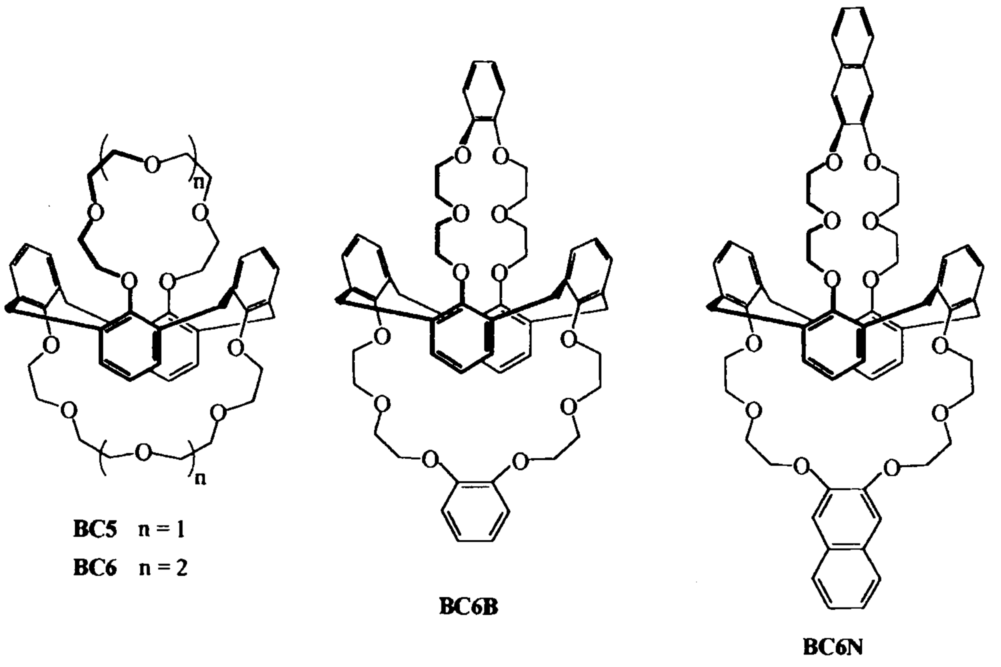

FIGURE 1 Chemical structures of the calix[4]arene *bis*(crowns) under study.

statistically disordered in the structure, which has been rationalized in terms of a distribution over four sites. Two positions, Ag1A and Ag2A, located in the two ether sites of the calixcrown, are predominant, with occupation factors refined to 0.871(3) and 0.73(1), and correspond mainly to an ethereal complexation, whereas the two other positions, Ag1B and Ag2B, correspond to increased polyhapto bonding. These latter positions are located on the same side of the calixarene than Ag1A and Ag2A, respectively, and they were given occupation factors constrained to sum up to unity with those of the corresponding predominant site. The molecular unit of **1** is represented in Figure 2, in which the two sets of positions have been separated on two different views for clarity, although of course the four possible (Ag1, Ag2) couples may presumably exist. Selected bond distances and angles around silver ions are given in Table I (bond lengths and angles in the calixarene moiety and counter-ions do not deviate significantly from the usual ones).

The two silver ions Ag1A and Ag2A are located in the ether loops, on the side opposite to the calixarene moiety. This bonding mode recalls what is observed in the complex of sodium ions with **BC6** [7]: in both cases, the cation is bonded to three ether oxygen atoms only, which is due to the size of those cations, too small for a good ligand/cation complementarity to be attained (ionic radii of 0.97 and 1.26 Å for Na$^+$ and Ag$^+$ respectively, to be compared to 1.61 Å for Cs$^+$, perfectly adapted to the cavity size of **BC6**). In spite of the ionic radius difference, the Ag —O distances are comparable to Na —O distances: the mean value is 2.6(1) Å in both cases. A search in the Cambridge Structural Database System (CSDS) [23] gives 45 structures with Ag —O (ether) bonds, and distances ranging from 2.258

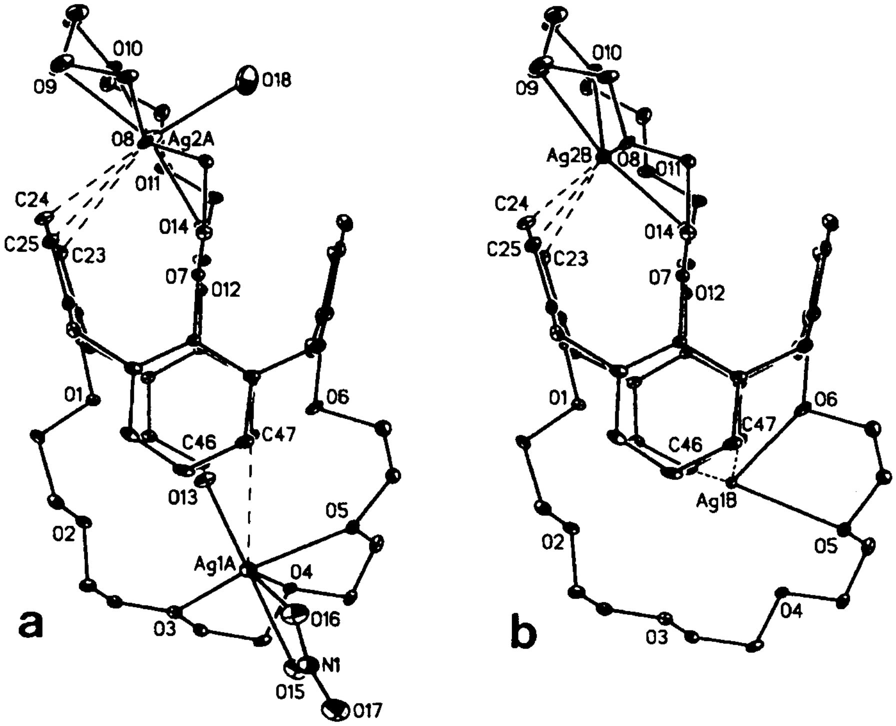

FIGURE 2 Molecular unit of 1. The two sets of disordered positions are separated for the sake of clarity: (a) predominant positions (mainly ethereal bonding); (b) secondary positions (ethereal plus polyhapto bonding). The hydrogen atoms, non-bonding nitrate ion and solvent molecule are omitted.

TABLE I Selected interatomic distances (Å) and torsion angles (°) in **1**

Ag1A—O1	5.085(5)	Ag1B—O1	3.772(7)
Ag1A—O2	3.843(5)	Ag1B—O2	3.705(5)
Ag1A—O3	2.619(5)	Ag1B—O3	3.796(8)
Ag1A—O4	2.618(5)	Ag1B—O4	3.603(8)
Ag1A—O5	2.535(5)	Ag1B—O5	2.688(7)
Ag1A—O6	3.904(5)	Ag1B—O6	2.332(7)
Ag1A—O13	2.257(6)	Ag1B—C46	2.758(9)
Ag1A—O15	2.452(8)	Ag1B—C47	2.514(9)
Ag1A—O16	2.685(8)		
Ag1A—C46	3.640(9)		
Ag1A—C47	3.765(6)		
Ag2A—O7	3.994(5)	Ag2B—O7	3.937(5)
Ag2A—O8	2.756(5)	Ag2B—O8	2.750(6)
Ag2A—O9	2.653(4)	Ag2B—O9	2.453(7)
Ag2A—O10	2.322(5)	Ag2B—O10	2.469(6)
Ag2A—O11	2.948(5)	Ag2B—O11	3.084(5)
Ag2A—O12	4.165(5)	Ag2B—O12	4.161(7)
Ag2A—O14	2.170(4)	Ag2B—O14	2.303(7)
Ag2A—O18	2.509(14)	Ag2B—O18	3.189(15)
Ag2A—C23	3.493(9)	Ag2B—C23	2.952(10)
Ag2A—C24	2.914(8)	Ag2B—C24	2.243(12)
Ag2A—C25	3.252(8)	Ag2B—C25	2.628(9)
O1—C1—C2—O2	−70.5	O7—C11—C12—O8	68.8
O2—C3—C4—O3	96.1	O8—C13—C14—O9	−66.5
O3—C5—C6—O4	−61.7	O9—C15—C16—O10	−61.6
O4—C7—C8—O5	62.2	O10—C17—C18—O11	70.8
O5—C9A—C10A—O6	75.3	O11—C19—C20—O12	−74.6
O5—C9B—C10B—O6	−89.3		

to 2.899 (mean value 2.555) Å, in agreement with the values determined here. Like in the sodium case, a water molecule completes the coordination sphere of Ag1A and Ag2A: those molecules are located between the facing phenyl rings of the calixarene and make possible hydrogen bonds with ether oxygen atoms (O13...O6 2.889, O14...O7 2.667, O14...O12 2.746 Å). The Ag—O(water) distances are slightly larger than the range obtained from the CSDS: 2.195 to 2.664 (mean value 2.460) Å; however, seven structures containing such bonds are reported only. One of the nitrate ion is asymmetrically bidentate, with distances in the range commonly observed (the 55 data from the CSDS lie in the range 2.136–2.738 (mean value 2.480) Å), while the second one is non-bonding, being replaced on Ag2A by a water molecule located outside the calixarene moiety (O18). Those two silver positions are rather far from the phenyl rings, the shorter contact being 2.914(8) Å, *i.e.*, larger than the sum of cation radius plus the π-electron cloud half-thickness (2.86 Å) [19].

The second position of Ag2, Ag2B, is slightly displaced towards one phenyl ring with respect to Ag2A. Ag2B is bonded to three ether oxygen atoms, with Ag—O distances comparable to the previous ones, but it cannot any more be considered to be bonded to O18. On the other hand, it is very close to three carbon atoms of the phenyl ring (mean Ag—C distance 2.6(3) Å), which may be considered as evidence of cation/π-electrons interactions. The Ag2B—C24 distance appears particularly short when compared to the Ag-aromatic ring distances observed in cyclophane, stilbene or calixarene complexes previously reported, which lie in the range 2.39–2.70 Å, which may be due to the rather low precision due to the inherent disorder of the present structure.

The case of Ag1B is more remarkable since this ion is located inside the calixarene cavity, in a position near that of the water molecule O13 (which has been assumed partially occupied, in association with Ag1A and with the same occupation factor). This cation is bonded to the two ether oxygen atoms nearer to the calixarene only (mean Ag —O distance 2.5(2) Å) and, like Ag2B, makes short contacts with three carbon atoms (mean Ag —C distance 2.6(2) Å). This cation is thus, although asymetrically bonded to only one of the two facing phenyl rings of the 1,3-*alternate* conformation, close to previous cases with calixarenes in such a conformation [17–20].

The Ag —C distances suggest that the cations in the present structure are not bound to aromatic rings centres, but to their edges, indicating interactions with specific C = C double bonds, as previously noticed [19].

The conformations of the ether chains can be described by the sequence of the signs of *gauche* O —C —C —O torsion angles given in Table I. The crown corresponding to atoms O1...O6 gives the sequence $g^-g^+g^-g^+(g^-$ or $g^+)$, the last sign associated with the disordered part, and the other crown (O7...O12) gives $g^+g^-g^-g^+g^-$, with some deviations of the *anti* C —O —C —C torsion angles from their ideal value. The conformation with alternated plus and minus signs is the most frequently observed in **BC6** complexes [6]. The other two conformations present here (the second of the first crown and that of the second crown) are the same as those observed in the sodium complex, which is further evidence of the similarities between those two complexes.

Complexation in Solution

The complexation behaviour of **BC6** towards Ag^+ has been followed by biphasic extraction of the corresponding picrate from water into dichloromethane and by complexation experiments performed in two homogeneous media, methanol and acetonitrile. The results are given in Table II, which also includes, for comparison, values for the related **BC5**, **BC6B** and **BC6N** ligands. The following observations can be made:

(i) Silver picrate is well extracted by **BC6** ($\%E = 40.6$), but slightly less than by **BC5** ($\%E = 45.7$). The substitution of the crown parts either by a 1,2-phenylene or a 2,3-naphthylene group leads to a substantial decrease of the extraction level, $\%E$ being about 18 for both **BC6B** and **BC6N**. No such difference in behaviour between **BC6** and its

TABLE II Binding properties of **BC6** and related calix[4]arene *bis*(crowns) towards Ag^+: percentage of extraction from water into dichloromethane, stability constants ($\log\beta \pm \sigma_{n-1}$) in methanol and acetonitrile and thermodynamic parameters of complexation in methanol

	Species	BC6	BC6B	BC6N	BC5
$\%E$		40.6±0.1	18.0 ± 0.1	18.15 ± 0.06	45.7 ± 0.2
Log β_{xy} (MeOH)	1:1	4.5 ± 0.1	^{a}	^{a}	5.58 ± 0.01^{b}
	2:1	–	^{a}	^{a}	9.34 ± 0.01^{b}
$-\Delta G_{xy}$ (kJ mol^{-1})	1:1	25.4 ± 0.5	–	–	31.79 ± 0.06
	2:1	–			53.22 ± 0.06
$-\Delta H_{xy}$ (kJ mol^{-1})	1:1	26.5 ± 0.1	–	–	29.8 ± 0.2
	2:1	–			41 ± 1
$T\Delta S_{xy}$ (kJ mol^{-1})	1:1	− 1.1 ± 0.6	–	–	2.0 ± 0.3
	2:1	–			12 ± 1
ΔS_{xy} (JK^{-1} mol^{-1})	1:1	4 ± 2			7 ± 1
	2:1	–			40 ± 3
Log β_{xy} (MeCN)	1:1	≤ 1	2.50 ± 0.03	4.1 ± 0.2	2.25 ± 0.01

[a] ligand not soluble enough in methanol.
[b] from Ref. [3].

substituted counterparts was observed with alkali metal ions.

(ii) The formation of a 1:1 complex has been established in methanol by both spectrophotometry and potentiometry. The values obtained by the two methods are in good agreement. The corresponding mean value, given in Table II, is slightly lower than the value derived from potentiometric measurements already published for **BC5** [3]. It thus appears that Ag^+ is better extracted and complexed by **BC5** than by **BC6**. However, by contrast to the results obtained with **BC5** and to the isolation of a 2:1 binuclear species of **BC6** in the solid state, no evidence for the formation of such a complex is found with **BC6** under our experimental conditions.

(iii) The stabilization of the silver complex in methanol is enthalpy driven ($-\Delta H > 0$ and $T\Delta S \approx 0$). However the enthalpy change ($-\Delta H = 26.5\,\text{kJ mol}^{-1}$) is much lower than the values observed for the larger alkali metal ions K^+, Rb^+ and Cs^+ for which $31.7 \leq -\Delta H \leq 56.2\,\text{kJ mol}^{-1}$. This is consistent with the fact that only some of the oxygen donor atoms of the crown moiety may be involved in the complexation, as suggested by the crystal structure of the binuclear complex. The higher stability of the silver 1:1 complex of **BC5** is due to more favourable enthalpy and entropy terms, which indicate certainly a higher degree of cation/ligand size complementarity.

(iv) As expected for silver complexes in acetonitrile, stability constants determined in this solvent are very low. An upper limit of 1 log unit only could be obtained for **BC6**. However, higher values could be determined with the other ligands which enable the comparison between the four calix[4] *bis* (crowns), as all these compounds are soluble enough in this solvent. Contrary to the expectations made on the basis of extraction results, **BC6N** is the best complexing agent for Ag^+ in acetonitrile. The higher complex stability of the substituted derivatives **BC6B** and **BC6N** may be explained by the increased rigidification of these molecules through substitution of the crown segment and possible interaction between the cation and these two aromatic substituents. The decrease in extraction level when going from **BC6** to **BC6B** and **BC6N** shows without any doubt the unfavourable effect of the crown substituents on the efficiency of extraction of Ag^+Pic^-. This result could be explained by a greater degree of steric hindrance for the formation of the ion pair Ag^+LPic^-, when L is **BC6B** or **BC6N**.

EXPERIMENTAL

Synthesis

0.15 mmol of calix[4]arene *bis*(crown-6), synthesized as already reported [1] was dissolved in nitromethane and a large excess of $AgNO_3$ (1 mmol) added. After 48 hours at 70°C, the unreacted $AgNO_3$ was filtered off. Recrystallization of the product from hot dimethylformamide yielded colourless crystals of **1**, moderately light-sensitive and suitable for X-ray crystallography.

Crystal Data

Ag_2**BC6**$(NO_3)_2(H_2O)_{1+x}\cdot(DMF)_{0.5}$, with x refined to 0.871(3) (**1**), $Ag_2O_{20.37}N_{2.5}C_{49.5}H_{66.74}$, $M = 1238.45$; monoclinic, space group $C2$, $a = 33.598(2)$, $b = 11.4711(3)$, $c = 13.7755(7)$ Å, $\beta = 104.585(2)°$; $V = 5138(2)$ Å^3; $Z = 4$; $D_x = 1.601$ g cm^{-3}; $\mu = 0.844\,\text{mm}^{-1}$; $F(000) = 2553$; crystal size $0.30 \times 0.30 \times 0.25$ mm.

Data Collection, Structure Determination and Refinement

Two data sets were recorded on two different crystals and the structure solved for each of them. The results were identical and the best one is reported in the following. The diffraction experiment was performed with a Nonius Kappa-CCD area detector diffractometer using graphite monochromated MoK_α radiation (0.71073 Å). The crystal was introduced in a Lindemann glass capillary. The lattice parameters were determined from ten images recorded with 1°ϕ-scans. The data were recorded at 123 K. A 180° range in ϕ was scanned with 2° steps. The crystal-to-detector distance was fixed at 28 mm. The data were processed with the HKL package [24]. No absorption correction was done. The structure was solved with SIR-92 [25] and refined by full-matrix least-squares on F^2 (all reflections unless 142 with strongly negative F^2 values were used) with SHELXTL [26]. The solvent DMF molecule is located near a binary axis; being unstable on refinement, it has been fixed with a 0.5 occupation. Two carbon atoms of a crown ether chain were found disordered over two positions. Hydrogen atoms of the calixarene moiety (unless those of the disordered part) were included as riding atoms, with thermal parameters equal to 1.2 times those of the attached carbon atoms. The correct enantiomorph was determined from the Flack parameter [27], which was 0.00(3). Analytical scattering factors for neutral atoms were corrected for the anomalous dispersion terms $\Delta f'$ and $\Delta f''$. 10401 unique observations, out of 20055 measured reflections ($R_{\text{int.}} = 0.057$), were used and 660 parameters refined (anisotropic displacement parameters for all non-hydrogen atoms, unless the disordered parts and the solvent molecule, 12 soft restraints applied). The extinction coefficient was refined to 0.0014(2). The final R values were $R_1 = 0.064$ ($\sum||F_o| - |F_c||/\sum|F_o|$, calculated on 6514 'observed' $[I > 2\sigma(I)]$ reflections) and $wR_2 = 0.213$ ($\{\sum[w(F_o^2 - F_c^2)^2]/[\sum wF_o^4]\}^{1/2}$ with $w = [\sigma^2(F_o^2) + (0.1041P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$). The goodness-of-fit was $S = 1.19$ ($\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where n and p are the number of reflections and the number of parameters refined respectively). The maximum positive and negative residual densities were 1.17 (near the solvent molecule) and -0.84 eÅ^{-3}.

Complexation Studies

The percentage of silver picrate extracted from water into dichloromethane has been determined at 20°C according to Pedersen's procedure. The concentrations of silver picrate in the aqueous phase and of the calixarene in the organic phase were both equal to 2.5×10^{-4} M. The experimental details and the preparation of the silver picrate have been previously reported [3, 28].

The stability constants β_{xy} equal to the concentration ratios $[Ag_xL_y{}^+]/([Ag^+]^x[L]^y)$ have been determined at 25°C in methanol by absorption spectrophotometry and potentiometry using a silver electrode with **BC6** and in acetonitrile by spectrophotometry with **BC6**, **BC6B**, **BC6N** and **BC5**. The experimental procedures have been previously described in detail [3]. The ionic strength was maintained at 10^{-2} M by use of Et_4NClO_4 (Fluka, purum), recrystallized twice from water and dried under vacuum at ambient temperature for 48 h. The metal salt $AgClO_4$ (Fluka, puriss.) was dried at ambient temperature for 24 h before use.

The enthalpies of complexation ΔH_{xy} have been determined by calorimetric titrations at 25°C using a Tronac 450 calorimeter. The experiments have been described in detail elsewhere [3]. The corresponding entropies of complexation ΔS_{xy} were derived from the expression $\Delta G_{xy} = \Delta H_{xy} - T\Delta S_{xy}$, with $\Delta G = -\text{RTLn}\,\beta$.

All the complexation measurements have been interpreted with the numerical program Sirko [29].

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