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Cyclodimethylsiloxane $(Me_2SiO)_m$ (m = 3–6) Ring Transformations on Reactions with $AgSbF_6$; Crystal Structure of $Ag(Me_2SiO)_7SbF_6$

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The reaction of D_m ($D = Me_2SiO$, m = 3–6) with silver hexafluoroantimonate in liquid SO_2 affords a mixture of AgD_nSbF_6 (n = 6–8) complexes. Upon the addition of CH_3CN, Ag^+-directed ring transformations are effected, which allows for the isolation of neat D_n (n = 6–8). The AgD_n^+ cations are rare examples of Lewis acid donor complexes of silicon ethers and Ag^+ oxygen donor complexes, and their isolation implies that numerous metal cation cyclosiloxanes can be prepared from readily available starting materials.

We recently reported the preparation of Li^+-cyclodimethylsiloxane host–guest cations directly from their components[1] and provided rare examples of silicon ethers behaving as Lewis bases as shown in Equation (1). Their structures imply that cyclodimethylsiloxanes (D_5 and D_6, $D = Me_2SiO$) act as pseudo crown ethers. Apart from alkali metal cations (Li^+ and $K^{+[2]}$) with large anions, no other examples of a metal-cation–siloxane adduct have been reported. Metal-cation–siloxane salt formation is favored by large anions, which minimizes the unfavorable lattice-energy changes. Therefore, the question as to whether the formation of the complexes could be extended to the use of commercially available salts with smaller anions as the starting materials remains. The Ag^+ cation is regarded as a soft Lewis acid[3] and has a low affinity to oxygen donor ligands.[4] Nevertheless, we report below the first examples of the transition-metal-cation–siloxane SbF_6^- salts of AgD_n^+ (n = 6–8) formed by the reactions of D_m (m = 3–6) with $AgSbF_6$ in liquid SO_2. Unlike the Li[Al] case, transformation of the siloxane rings occur with Ag^+ acting as a template for the formation of the most thermodynamically stable metal-cation–cyclodimethylsiloxane complex. The formation of macrocyclic ethers by the reaction of $AgAsF_6$ with $(CH_2O)_3$ or ethylene oxide was described by Roesky and his coworkers.[5] However, no similar ring transformation reactions of cyclodimethylsiloxanes under mild conditions have been previously reported.[6] Ring-opening polymerization of D_m (m = 3–6) has been widely investigated, and these results are also of interest in this context.

$$\mathrm{Li[Al]} + \mathrm{D}_m \xrightarrow[\text{r.t.}]{\mathrm{CH_2Cl_2}} \mathrm{LiD}_m\mathrm{[Al]} \qquad (1)$$

$$[\mathrm{Al}] = \mathrm{Al(OC(CF_3)_3)_4},\ m = 5 \text{ or } 6;$$
$$= \mathrm{Al(OC(CF_3)_2Ph)_4},\ m = 6$$

The reaction of excess $AgSbF_6$ with D_5 (1.4:1) in liquid SO_2 affords a colorless, highly hygroscopic solubilized product. When a saturated SO_2 solution of the product is cooled, a colorless crystalline material is afforded. Several single-crystals were identified by X-ray diffraction analysis as AgD_7SbF_6. However, the mass spectrum of the material showed fragments which can be attributed to $(D_6 - Me)^+$ and $(D_7 - Me)^+$. This implies that the crystalline material was a mixture of AgD_7SbF_6 and AgD_6SbF_6. Addition of a large excess of CH_3CN to the solubilized product led to a two-phase liquid. GC–MS analysis of the upper oily phase showed three main components: D_6, D_7 (3.4:1), and D_8 (Figure 1). The amount of D_8 present in the sample was very small in comparison with that of D_6 and D_7 (Figure 1c),[7] but its presence implies that a small amount of AgD_8SbF_6 was part of the mixture. The composition of the product was further confirmed by in situ $^{29}Si\{^1H\}$ NMR (Figure 1a) of the reaction of $AgSbF_6$ with D_5 (1.5:1). Three peaks (–13.585 $[AgD_7^+]$, –14.187 $[AgD_6^+]$, –12.83 ppm $[AgD_8^+]$) in a molar ratio of $AgD_7^+/AgD_6^+/AgD_8^+$ = 3.7:1:0.2 were found in the spectrum, which is consistent with the GC results (D_7/D_6 = 3.4:1). The change in the intensity of the peaks in the $^{29}Si\{^1H\}$ NMR spectrum with temperature implies that an equilibrium in liquid SO_2 exists: $2AgD_7^+ \rightleftarrows AgD_6^+ + AgD_8^+$ (Supporting Information, Figure S2.3). The $^{29}Si\{^1H\}$ NMR spectrum (in SO_2, Figure 1b) of the solution obtained after the addition of an excess amount of CH_3CN showed D_7 (–23.09 ppm) and D_6

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(–22.42 ppm) with traces of D_4 (–20.67 ppm) and D_5 (–21.89 ppm).[8] The reaction of $AgSbF_6$ with D_5 leads to the ring transformation of D_5 to D_6, and D_7 can be expressed as shown in Scheme 1. The separate reactions of excess $AgSbF_6$ with D_3, D_4, and D_6 gave similar results (Supporting Information, Figure S2.4). Thus, these AgD_n^+ (n = 6–8) cations are intermediates in cyclosiloxane ring transformations. The AgD_nSbF_6 complexes slowly decompose in SO_2 solutions to afford Me_2SiF_2, $(MeFSi)_2O$, $Me_2SiFOMe_2SiOSiFMe_2$, and $(Me_2SiFOMe_2SiF)_2O$ (Supporting Information, Figure S2.5).[9]

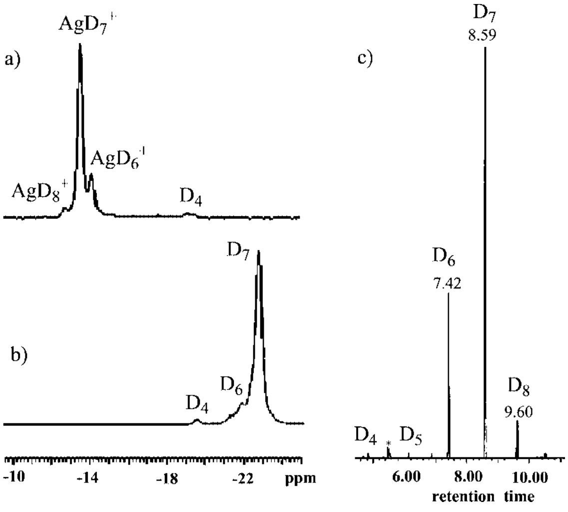


Figure 1. a) In situ $^{29}Si\{^1H\}$ NMR spectrum of the reaction of $AgSbF_6$ + D_5 (1.5:1) in liquid SO_2; b) in situ $^{29}Si\{^1H\}$ NMR spectrum after the addition of excess CH_3CN into the $AgSbF_6$ + D_5 (1.5:1) mixture in liquid SO_2; c) GC of the oily phase upon the addition of CH_3CN onto the solid product of the $AgSbF_6$ + D_5 (1.4:1) mixture in liquid SO_2 (The peak marked with * is due to an unidentified siloxane chain or rearranged siloxane ring).

Scheme 1.

The solid-state structure[10] of AgD_7SbF_6 (Figure 2) shows discrete AgD_7^+ cations and SbF_6^- anions connected by four weak Ag–F contacts {4 × [2.785(2) Å, 0.070 v.u.]}[11] which forms a chain along the *c*-axis (Figure 2c). The Ag atom coordinates with five oxygen atoms from D_7; three of these interactions are strong {Ag–O1 2.489(2) Å, 0.174 v.u.; 2 × [Ag–O4 2.553(1) Å, 0.146 v.u.]} in comparison with the Ag–O distances in $[(CH_2O)_6Ag_2]^{2+}$ and $Ag(12\text{-crown-}4)_2^+$ {6 × [2.458(5) Å, 0.188 v.u.] and 8 × [2.57(1) Å, 0.137 v.u.]}. Two of the Ag–O2 contacts are weak {2 × [2.811(1) Å, 0.073 v.u.]}. There are no significant contacts between the Ag and the O3 atoms {2 × [3.601(1) Å, 0.0086 v. u.]}. The sum of the bond valences (0.909 v.u.) of all the Ag–O contacts [0.174 + (0.146 × 2) + (0.073 × 2) + (0.0086 × 2) = 0.629 v.u.] and the Ag–F contacts (0.070 × 4 = 0.280 v.u.) correspond to one positive charge on Ag. The Si_7O_7 framework and the Ag atom are approximately planar, and the AgD_7^+ has an overall crystallographic C_{2v} symmetry.[12] This is different from the approximate D_{7h} symmetry found for KD_7^+ where K^+ is coplanar with the ring and interacts with all seven oxygen atoms of the cyclosiloxane ring. Near-planar pentadentate silver(I) complexes have been reported,[13] but this coordination mode is not common for silver(I) complexes. These complexes usually adopt a linear or octahedral coordination geometry.[4] The oxygen atoms that are not bonded to silver have Si–O bond lengths of 1.608 (2) Å (average), which is significantly shorter than the Si–O bond lengths for the oxygen atoms [1.636(1) Å, average] that are bonded to silver. This is similar to the situation for LiD_6^+. The average Si–O–Si angle at the coordinated O atoms, 144.1(1)°, is much smaller than that at the noncoordinated O atoms, 166.9(1)°. To the best of our knowledge, this Si–O–Si angle [166.9(1)°] is the largest reported among the Si–O–Si angles in cyclodimethylsiloxane. The nature of the bonding in AgD_7^+ is likely similar to that previously described in LiD_6^+, the differences are currently under investigation.

Some of the steps in a tentative Ag^+-directed ring transformation process are shown in Scheme 2. Coordination of Ag^+ to D_m lengthens and weakens the Si–O bond and induces a higher positive charge on silicon. Abstraction of F^- from SbF_6^- [fluoride ion affinity of SbF_5 (g) = 514 or 503 kJ·mol^{-1}][14] is therefore promoted and is driven by the formation of the Si–F bond (bond enthalpy of Si–F = 582 kJ·mol^{-1}),[15] which leads to the formation of the $FSiMe_2(OSiMe_2)_{m-2}OSiMe_2O^-$ anion. This anion can react further with D_m or AgD_n^+, which can lead to larger chain anions. These chain anions can then attack the silicon atoms to afford the most thermodynamically favored AgD_n^+ species (e.g. AgD_7^+ is more stable than AgD_6^+ [$Ag^+ (g) + 1.4\ D_5 (g) \rightarrow AgD_7^+ (g)$, $\Delta H = -439$ kJ·mol^{-1}; $Ag^+ (g) + 1.2\ D_5 (g) \rightarrow AgD_6^+ (g)$, $\Delta H = -414$ kJ·mol^{-1}].[16] The changes in the intensities of the AgD_n^+ (n = 6–8) signals with temperature in the $^{29}Si\{^1H\}$ NMR spectra (Supporting Information, Figure S2.3) imply that the system is in thermodynamic equilibrium. A cation-induced ring-opening mechanism has been established for base-initiated cyclodimethylsiloxane ring-opening polymerization. Alkali metal cyclodimethylsiloxane adducts are proposed as the intermediates; the mechanism is supported by the structure of AgD_7^+ and the detection of AgD_n^+ (n = 6–8) in this study.

This work implies that numerous salts of metal cyclodimethylsiloxane complexes can be prepared from commercially available starting materials. Cyclosiloxanes are believed to act as pseudo crown ethers. The work also suggests that other polycyclosiloxanes may be prepared if the metal cation is tailored in size. The size and nature of the anion, along with related ring transformations (e.g. cyclophosphazenes), may also be affected by $AgSbF_6$ or related salts.

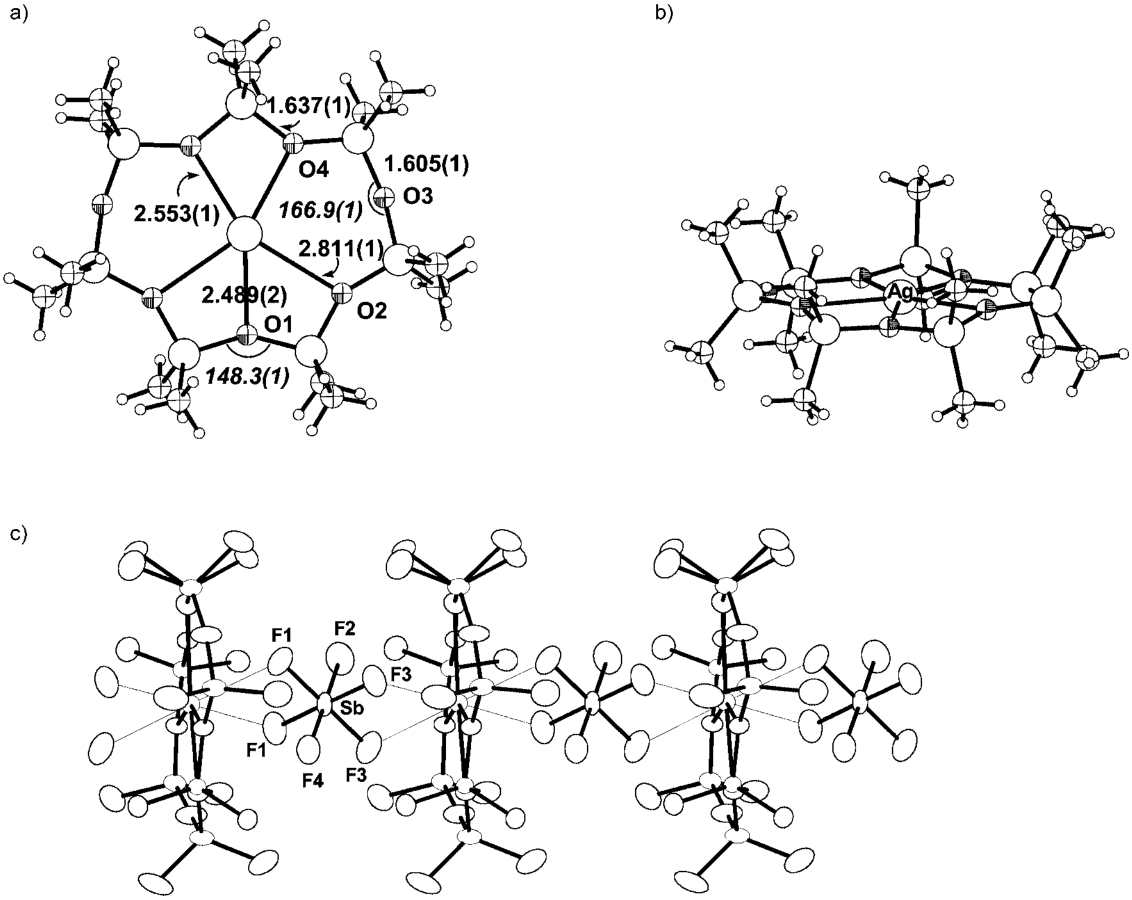
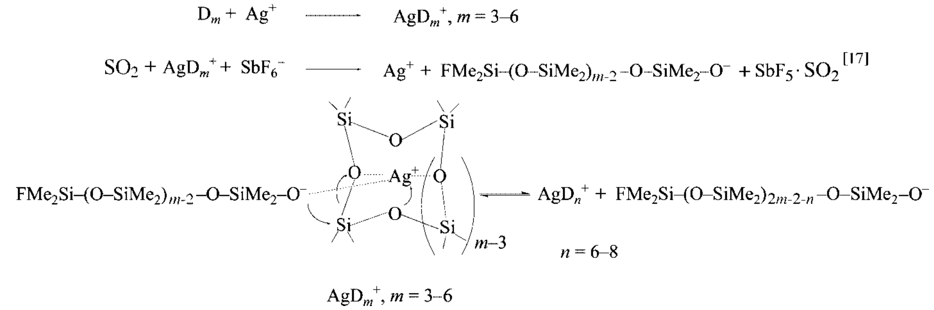


Figure 2. a) A top-view of AgD_7^+(bond length [Å], bond angle [°]); b) a side-view of AgD_7^+; c) a view of AgD_7SbF_6 along the *c*-axis (bond valences were unlined and hydrogen atoms were omitted for clarity).



Scheme 2.

Experimental Section

Reaction of $AgSbF_6$ with D_5 (mole ratio $AgSbF_6/D_5$ = 1.4:1) To Afford Single-Crystals of AgD_7SbF_6: $AgSbF_6$ (1.237 g, 3.6 mmol) in one tube (OD 1.5 cm) of a two-tube (Pyrex), two-valve (Teflon in glass) vessel with an incorporated medium frit was treated with $(Me_2SiO)_5$ (1 mL, 2.58 mmol). The vessel was cooled in liquid N_2 and degassed. SO_2 (7 mL) was distilled onto the mixture, and the reaction was warmed to room temperature. A small amount of colorless precipitate was then observed over a clear solution. This mixture was stirred overnight at 5 °C and then filtered. Removal of the volatiles afforded a colorless solubilized product (1.863 g) and a very small amount of colorless insoluble product. Insoluble product: IR (KBr, Nujol Mull, room temp.): ṽ = 3488 (wb), 2921 (s), 1613 (w), 1458 (s), 1377 (s), 1264 (s), 1061 (sb), 897 (s), 809 (s), 667 (s), 632 (m), 476 (m) cm^{-1}. Scanning electron microscopy-energy dispersive angle X-ray (SEM-EDAX) analysis showed that the insoluble product probably contained SiO_2, Sb_2O_3, $SbF_3 \cdot SbF_5$, and AgF. The solubilized product that was obtained in similar reactions was used in the following workups: i) C*rystallization*: SO_2 (about 8 g) was added to the solubilized products (1.65 g) in a two-tube vessel. The resulting solution was concentrated until saturation and then cooled to 5 °C overnight, to afford a colorless crystalline product. The vessel was cooled to –78 °C and one valve opened. Crystals were quickly picked out of the solution with a miniature nickel spoon.[18] Single-crystals suitable for X-ray diffraction were coated with paratone-N oil, mounted with a glass fiber, and frozen in liquid nitrogen while mounted on the goniometer. The crystalline product was collected in dry box (0.375 g, 23%). M.p: 150 °C (decomp.). IR (KBr, neat, room temp.): ṽ = 2959 (m), 2903 (w), 1605 (wb), 1446 (wb), 1412 (w), 1377 (w), 1262 (s), 1056 (vs), 859 (m), 799 (vs), 701 (m), 658 (s, SbF_6^-), 536 (w), 506 (w), 382 (s, SbF_6^-) cm^{-1}. EI-MS (60 ev): *m/z* (%) = 503 (25) $[D_7 - 15]^+$, 429 (12) $[D_6 - 15]^+$. ii) *Displacement*: CH_3CN (3 mL) was condensed onto the solubilized product (2 g) in a 10 mm-NMR tube glass-blown onto a valve (Teflon in glass) to afford a two-layer solution. The upper layer of oily liquid was removed by syringe (0.6 mL). GC–MS: *m/z* (%) = 429 (21) $[D_6 - 15]^+$, 503 (100) $[D_7 - 15]^+$, 429 (21) $[D_6 - 15]^+$, 577 (9) $[D_8 - 15]^+$. GC-FID: % = 23 (D_6), 77 (D_7).

In situ NMR Reaction of $AgSbF_6$ with D_5 (1.5:1): SO_2 (4 mL) was condensed onto $AgSbF_6$ (2.018 g, 5.87 mmol) and D_5 (1.5 mL, 3.87 mmol) in a 10 mm NMR tube described above and sonicated in ice water for 0.5 h to afford a colorless solution over a small amount of colorless precipitate. $^{29}Si\{^1H\}$ NMR (79.4 MHz, SO_2, 25 °C): δ = –14.187 (s, AgD_6^+), –13.585 (s, AgD_7^+), –12.83 (s, AgD_8^+) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, SO_2, 5 °C):δ = –14.106 (s, AgD_6^+), –13.502 (s, AgD_7^+), –12.01 (s, AgD_8^+) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, SO_2, –5 °C): δ = –14.03 (s, shoulder, AgD_6^+), –13.456 (s, AgD_7^+), –12.02 (s, AgD_8^+) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, SO_2, –15 °C): δ = –13.403 (br. s, AgD_7^+) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, SO_2, –40 °C): δ = –13.547 (s, AgD_7^+), –12.379 (s, AgD_8^+) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, SO_2, –70 °C): δ = –13.315 (s, AgD_7^+), –12.196 (s, AgD_8^+) ppm. ^1H NMR (400 MHz, SO_2, 25 °C): δ = 0.225 (s, $SiMe_2$) ppm; $^{13}C\{^1H\}$ (100 MHz, SO_2, 25 °C): δ = 0.414 (s, $SiMe_2$) ppm. CH_3CN (ca. 1.5 mL) was then condensed into this solution and sonicated in ice water for 1 h. $^{29}Si\{^1H\}$ NMR (79.4 MHz, SO_2/CH_3CN, 25 °C): δ = –23.093 (s, D_7), –22.415 (s, D_6), –21.90 (s, D_5), –20.668 (s, D_4) ppm. ^1H NMR (400 MHz, SO_2, 25 °C): δ = 1.350 (s, CH_3CN), –0.693 (s, $SiMe_2$) ppm; $^{13}C\{^1H\}$ (100 MHz, SO_2, 25 °C): δ = 119.027 (s, $CH_3{}^{13}CN$), 1.586 (m, $^{13}CH_3CN$ and $SiMe_2$) ppm.

Supporting Information (see footnote on the first page of this article): General experimental techniques, in situ ^{29}Si NMR reactions of $AgSbF_6$ with D_m (*m* = 3, 4, and 6) in liquid SO_2, FT-IR, MS, and $^{29}Si\{^1H\}$ NMR spectra, and full details of the crystal structure of AgD_7SbF_6 as well as a comparison with KD_7^+.

Acknowledgements

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[8] D_8 ring was not detected likely because of the low concentration and its signals overlapped with those of D_7. $^{29}Si\{^1H\}$ NMR [79.4 MHz, SO_2]: δ = –19.64 (D_4), –21.67 (D_5), –22.69 (D_6) ppm, this work. For $^{29}Si\{^1H\}$ NMR (19.87 MHz, C_6D_6): δ = –9.88 (D_3), –23.03 (D_7),–22.98 (D_8) ppm, see D. J. Burton, R. K. Harris, K. Dodgson, C. J. Pellow, J. A. Semlyen, *Polym. Commun.* **1983**, *9*, 278.

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[10] X-ray structure determination of AgD_7SbF_6: Bruker AXS P4/SMART 1000 diffractometer with graphite monochrometer, T = 173 ± 1 K. Unit cell determination: absorption correction by SADABS, direct methods, refinement with SHELXTL 6.14. Space group = $P21/m$, a = 7.4272(6) Å, b = 20.8687(16) Å, c = 11.4437(9) Å, β = 102.484(1)°, V = 1731.8(2) Å^3, Z = 2, D_{calc} = 1.654 Mg/m^3, $2\theta_{max}$ = 55.0°, reflections: 12112 collected, 3995 independent, 823 parameters, $R1$ ($I > 2\theta$) = 0.0206, $R1$ (all data) = 0.0272. CCDC-610025 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] The bond valences *s* (in valence units v.u.) are defined as $s = \exp[(R_o - R)/B]$, where R is the observed distance, R_o is the covalent bond length of the bond (bond order = 1; for Ag–F, R_o = 1.80 Å; for Ag–O, R_o = 1.84 Å), and B is an empirical parameter set to 0.37. a) I. D. Brown in *Structure and Bonding in Crystals*, vol. 2 (Eds.: M. O'Keefe, A. Navrotsky), Academic Press, London, **1981**; b) I. D. Brown, *The Chemical Bond in Inorganic Chemistry – The Bond Valence Model*, Oxford University Press, Oxford, **2002**.

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