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Synthesis and crystal structures of silver(I) bridged tetra-phenyl-pyrylium complexes from tetraphenyl-cyclopentadiene

Gui Ling Ning [a,*], Xin Cheng Li [a], Wei Tao Gong [a], Megumu Munakata [b], Masahiko Maekawa [b]

[a] State Key Laboratory of fine Chemicals, Dalian University of Technology, Zhongshan Road 158, Dalian 116012, PR China
[b] Department of Chemistry, Kinki University, Osaka 577, Japan

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Abstract

Reactions of silver(I) perchlorate with tetraphenyl-cyclopentadiene ($Ph_4H_2C_5$) have isolated two novel silver(I) bridged tetraphenyl-pyrylium complexes: $[Ag(ClO_4)(Ph_4HC_5O^+)](ClO_4)^-$ (**1**) and $[Ag(ClO_4)(H_2O)(Ph_4HC_5O^+)](ClO_4{}^-)$ (**2**), depending on moisture-content of the reactants. Structure studies using single-crystal X-ray diffraction have showed that complex **1** contains a distorted tetrahedral metal center bridging two neighboring peripheral phenyl rings of one pyrylium cation and two perchlorate anions, whereas **2** involves a three-coordinate metal ion interacting with a pair of phenyl rings and one water molecule, leaving two perchlorate anions free from coordination. For both complexes, the precursor ligand $Ph_4H_2C_5$ undergoes a ring-enlargement reaction, forming a six-membered pyrylium cation. The fundamentals of the synthesis, structure characterization and some properties are discussed.

Keywords: Pyrylium; Silver(I) perchlorate; Complex; Tetraphenylcyclopentadiene

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1. Introduction

Pyrylium salts have opened up broad prospects in commercial applications owing to their fluorescence and charge-transfer properties [1–4]. The peculiarities in the photophysical and electrochemical characteristics are attributable to the substitution patterns of the pyrylium ring [1,4–6]. Although a large number of differently substituted pyrylium salts have been synthesized and studied, almost all substitution species are composed of organic groups or motifs [4–7]. The investigations of introducing metal ions into the substitution system for some potential properties are very limited [8]. In this paper, we exhibit two silver(I) bridged tetraphenyl-pyrylium complexes synthesized from tetra-phenyl-cyclopentadiene.

During the course of our exploration of silver(I) complexes with polycyclic hydrocarbons for functional materials [9,10], we found that the five-membered cyclopentadiene ring of phenyl substituted cyclopentadienes, such as tri-, tetra- and/or penta-phenyl-cyclopentadiene, could be converted to six-membered pyrylium ring by interacting with silver(I) perchlorate. The characterizations and formation mechanism of these pyrylium salts have been published in our preliminary reports [11]. Interestingly, among these compounds, only tetra-phenyl-pyrylium cation involved a silver(I) ion in its peripheral phenyl rings despite the same reaction condition and process being followed. Furthermore, by changing

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[*] Corresponding author. Tel.:/fax: +86 41188993609.
E-mail address: ninggl@dlut.edu.cn (G.L. Ning).

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the moisture-content of $Ph_4H_2C_5$ [1], another silver(I) coordination pattern was also isolated. We report here, in detail, the synthesis, structural characterizations and some properties of these two complexes.

2. Experimental

2.1. General procedures

All reactions and manipulations were carried out under an argon atmosphere using usual Schlenk techniques. Solvents were dried and distilled by using standard methods prior to use. Reagent grade 1,2,3,4-tetraphenylcyclopentadiene was purchased from Tokyo, Kasei Kogyou Co. Ltd., while silver(I) perchlorate monohydrate was from Aldrich. IR spectra were recorded as KBr disks on a JASCO FT-IR 460 spectrometer. ^1H NMR spectra were obtained on INOVA 400 for complex **1**, GSX 270 FT for complex **2** and $Ph_4H_2C_5$ precursor ligand. ^{13}C NMR spectra were recorded on INOVA 400. MS were measured on HP1100 for **1** and JEOL LMS-HX 100 for **2**. UV–Vis spectra were recorded on a Hitachi 150-20 spectrophotometer. Elemental analyses of complex **1** and **2** were performed by Dalian Institute of Chemical Physics, China Academy of Science and by the Department of Chemistry, Tokyo Metropolitan University, Japan, respectively.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared and handled with great care.

2.2. Synthesis

2.2.1. $[Ag(ClO_4)(Ph_4HC_5O^+)]ClO_4^-)$ (**1**)

To a solution of tetraphenyl-cyclopentadiene, $Ph_4H_2C_5$ (15 mg, 0.04 mmol), in a mixed solvent of CH_2Cl_2/toluene (3/1 in volume, 4 ml) was added $AgClO_4 \cdot H_2O$ (46 mg, 0.2 mmol). After being stirred for about 20 min, the resultant colorless solution was transferred to a 7-mm diameter glass tube and layered with *n*-hexane as a diffusion solvent. The glass tube was sealed under Ar and wrapped with aluminum foil. After standing at room temperature in the dark for about 6 weeks, X-ray quality yellow plate crystals of **1** were obtained, 26% in yield. IR, ν/cm^{-1}: 1594s (pyrylium ring skeleton), 1093vs and 1044vs ($\nu_{Cl–O}$). ^1H NMR [23 °C, $(CD_3)_2CO$, 400 MHz]: δ 9.96 (1H, s, pyrylium ring). Ms, *m*/*z*: 385.2. *Anal*. Calc. for $C_{29}H_{21}AgCl_2O_9$ (**1**): C, 50.27; H, 3.03. Found: C, 50.04; H, 3.08%.

2.2.2. $[Ag(ClO_4)(H_2O)(Ph_4HC_5O^+)](ClO_4^-)$ (**2**)

The brown column crystals of **2** were prepared in the same way as **1**, using $Ph_4H_2C_5 \cdot nH_2O$ (15 mg, 0.04 mmol) instead of $Ph_4H_2C_5$. $Ph_4H_2C_5$ is moisture-adsorbing substance and $Ph_4H_2C_5 \cdot nH_2O$ can be easily obtained by keeping the chemical in the air for 2–10 days. The increased moisture-content makes the reaction much easier. X-ray quality crystals of **2** were obtained after 2 weeks' standing of the glass tube, 41% in yield. IR, ν/cm^{-1}: 1597s (pyrylium ring skeleton), 1112vs ($\nu_{Cl–O}$). ^1H NMR [23 °C, $(CD_3)_2CO$, 270 MHz]: δ 9.89(1H, s, pyrylium ring). ^{13}C NMR [23 °C, $(CD_3)_2CO$, 400 MHz, δ in ppm]: 209.97, 206.20, 173.61, 170.55, 164.03 (5 signals). Ms, *m*/*z*: 385. *Anal*. Calc. for $C_{29}H_{23}AgCl_2O_{10}$ (**2**): C, 49.04; H, 3.26. Found: C, 48.36; H, 3.25%.

2.3. X-ray crystallography

The single crystal suitable for X-ray measurement was fixed on a glass fiber with adhesives. The diffraction data for the two complexes were collected at room temperature for **1** and 273.2 K for **2** on a Rigaku AFC7R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation. Space groups were selected on the basis of systematic absences and intensity statistics. Over the course of data collection, no decay correction was applied for the complexes. All intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods followed by subsequent Fourier-difference calculation and refined by a full-matrix least-squares analysis on *F* using the TEXAN package [12]. Hydrogen atoms of all of the two structures were introduced into their calculated positions; they were included, but not refined. Details of the X-ray experiments and crystal data are summarized in Table 1. Final atomic coordinates for all of the structures are given in the Supporting Information. The selected bond distances and angles for the two complexes are listed in Table 2.

3. Results and discussion

3.1. Synthesis, characterization and properties

The reactions of $Ph_4H_2C_5$ with silver(I) perchlorate in a mixed solvent of CH_2Cl_2/toluene afforded complexes **1** and **2**, depending on the moisture-content of $Ph_4H_2C_5$, Footnote 1. The synthesis of the two organometallics can be thought of as a type of combinatorial chemistry, achieved by simultaneous ligand modification and metal coordination reaction. It has been found in our studies that phenyl substituted cyclopentadienes did not form coordination complexes with silver perchlorate at normal conditions, although they proved a strong ability

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[1] For **2**, $Ph_4H_2C_5$ was exposed to the air with relative humidity 60–70% for more than 10 days at room temperature. While for **1**, the moisture-saturated $Ph_4H_2C_5$ were put into a drying box for 2–3 days before use.

Table 1
Crystallographic data

	1	2
Formula	$C_{29}H_{21}AgCl_2O_9$	$C_{29}H_{23}AgCl_2O_{10}$
Formula weight	692.25	710.27
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Temperature (K)	273.2	296.2
Unit cell dimensions		
a (Å)	10.567(1)	12.030(3)
b (Å)	17.999(1)	13.764(4)
c (Å)	14.7519(4)	17.662(6)
β (°)	99.4277(6)	93.25(3)
V (Å^3)	2767.8(3)	2919(1)
Z	4	4
F(0 0 0)	1392	1432
ρ_{calc} (g cm^{-3})	1.661	1.616
Radiation, λ(Mo Kα) (Å)	0.7107	0.7107
μ cm^{-1}	9.74	9.28
Number of data collected	6313	6699
Number of data in refinement	3823	2423
R_1	0.0592	0.059
wR_2	0.0845	0.170
GOF on F	2.255	1.785
ρ_{max}/ρ_{min} (e Å^{-3})	1.39/−0.85	0.8/−0.52

Table 2
Selected bond lengths (Å) and angles (°)

1			
Ag(1)–O(1)	2.404(6)	Ag(1)–O(5)	2.317(7)
Ag(1)–C(14)	2.523(7)	Ag(1)–C(20)	2.593(6)
Ag(1)–C(15)	2.772(7)	Ag(2)–C(21)	2.774(8)
C(1)–O(9)	1.353(6)	C(5)–O(9)	1.319(6)
C(1)–C(2)	1.354(7)	C(2)–C(3)	1.398(7)
C(3)–C(4)	1.416(7)	C(4)–C(5)	1.388(7)
O(1)–Ag(1)–C(14)	105.8(2)	O(1)–Ag(1)–C(20)	114.7(2)
O(5)–Ag(1)–C(14)	118.3(3)	O(5)–Ag(1)–C(20)	91.8(3)
O(1)–Ag(1)–O(5)	93.7(4)	C(14)–Ag(1)–C(20)	127.5(2)
C(1)–O(9)–C(5)	122.1(4)	O(9)–C(1)–C(2)	121.9(4)
C(1)–C(2)–C(3)	118.1(4)	C(2)–C(3)–C(4)	118.8(4)
C(3)–C(4)–C(5)	119.5(4)	C(4)–C(5)–O(9)	119.3(4)
2			
Ag(1)–O(2)	2.243(7)	Ag(1)–C(16)	2.677(10)
Ag(1)–C(21)	2.61(1)	Ag(1)–C(22)	2.53(1)
O(1)–C(1)	1.35(1)	O(1)–C(5)	1.35(1)
C(1)–C(2)	1.37(1)	C(2)–C(3)	1.39(1)
C(3)–C(4)	1.40(1)	C(4)–C(5)	1.33(1)
O(2)–Ag(1)–C(16)	86.1(3)	O(2)–Ag(1)–C(21)	132.9(3)
O(2)–Ag(1)–C(22)	151.4(3)	C(16)–Ag(1)–C(21)	131.3(3)
C(16)–Ag(1)–C(22)	122.0(3)	C(21)–Ag(1)–C(22)	31.1(3)
C(1)–O(1)–C(5)	120.7(8)	O(1)–C(1)–C(2)	118.9(9)
C(1)–C(2)–C(3)	120.1(8)	C(2)–C(3)–C(4)	119.6(8)
C(3)–C(4)–C(5)	117.3(9)	C(4)–C(5)–O(1)	123.3(8)

to undergo simple η^5-coordination with some transition-metal and lanthanide-metal ions, such as Gr, Fe, Ru, Co, Mo, Rh, Ni, Pd, Ge, Sn, Pb, W and Lu [13]. Compound **2** was isolated occasionally by using the moisture-adsorbed $Ph_4H_2C_5$ and $AgClO_4 \cdot H_2O$ in the mixed solvent. This motivated us to control the moisture-content of $Ph_4H_2C_5$, and thus complex **1** was obtained. Scheme 1 gives the equation for the reaction of $Ph_4H_2C_5$ with $AgClO_4$ in the presence of H_2O, which has been verified by our extensive study [11]. The reaction shows that the original five-membered cyclopentadiene-ring of $Ph_4H_2C_5$ is enlarged into six-membered pyrylium-ring by inserting an oxygen atom, and meanwhile a silver(I) ion is coordinated to its peripheral phenyl rings. Here, due to the fact that part of silver(I) ions act as an oxidant, an excess amount of silver(I) perchlorate has been used for the coordination. However, while silver(I) perchlorate decreases, the silver(I) coordinated pyrylium complex can also be obtained although part of $Ph_4H_2C_5$ remains. The bridged silver(I) ions in **1** and **2** cannot be removed by changing the amount of silver(I) perchlorate, or by solvent extraction.[2] In contrast, while using bi-, tri- or penta-phenyl-cyclopentadiene instead of $Ph_4H_2C_5$ in the reaction, only silver(I)-free pyrylium cations have been obtained, regardless of a large excess of silver(I) perchlorate used. The formation rate of the two complexes is dependent on the moisture-content. If all reactants were deeply dried before use, neither complex **1** nor **2** could be obtained. With partially dried $Ph_4H_2C_5$, in the case of **1**, the complex was formed very slowly, while for **2**, in which $Ph_4H_2C_5$ was exposed to the air with relative humidity 60–70% for more than 10 days at room temperature, the crystals were obtained much easier. However, if excess water were dropped in the reaction solution, making organic/inorganic phase separated, no crystals could be observed anymore, probably due to the instability of pyrylium cations in water [14]. On the other hand, without silver(I) ions, the reaction in Scheme 1 could not take place. Several other metal ions, such as Cu(I), Cu(II) and Au(I) ions, have been used in place of Ag(I) ion to investigate the reaction. However, there has been no pyrylium salt formed, although the reduced Cu/Au metals were observed. Here, silver(I) ion most likely functions as both a Lewis acid catalyst and an oxidant. It is noteworthy that the mixed solvent of CH_2Cl_2/toluene has to be used in the synthesis. Toluene is used to dissolve silver(I) perchlorate, whereas the polar CH_2Cl_2 probably serves as an acceptor to dissolve the formed pyrylium salts. Either of the solvents can make $Ph_4H_2C_5$ dissolved.

These two complexes are soluble in common polar organic solvents such as methanol, acetone or CH_2Cl_2. They are very stable in the open laboratory environment despite a little moisture-sensitivity at room temperature. However, they decomposed below 150 °C forming black powder.

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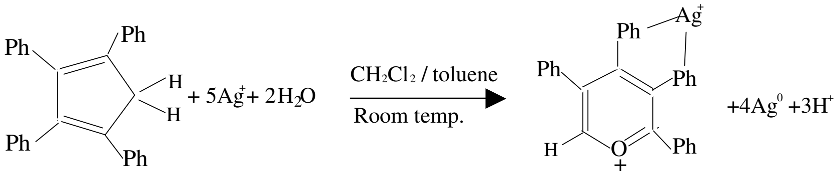
[2] Water and benzene were selected as the extracting solvents. By emerging these single crystals into either of the solvents for 24 h and then undergoing a chemical analysis, the released silver(I) ion from the crystals can be detected.



Scheme 1.

Characterization of the complexes was mainly based on X-ray diffraction studies. Nevertheless, IR, NMR, MS spectra and elemental analysis are good supplementary means to confirm incorporation of metal/perchlorate ions and formation of pyrylium cations. The strong absorption bands observed at 1093–1044 cm^{-1} for **1** and 1112 cm^{-1} for **2** in IR spectra indicate the presence of ClO_4^- [9,10], which do not exist in the spectrum of its precursor $Ph_4H_2C_5$. The strong split absorption in complex **1** at 1093–1044 cm^{-1}(νOCl) is consistent with coordination of the perchlorate oxygen to metal ion [10b,15]. According to the literature data [4a,18], the skeleton vibrations of the pyrylium ring are 1594 cm^{-1} for **1** and 1597 cm^{-1} for **2**, respectively, although they exhibit obvious downfield shifts. The changed wave numbers may be attributable to the substitution or coordination pattern of the pyrylium ring [4a]. The ^1H NMR spectra of **1** and **2** together with their precursor ligand in $(CD_3)_2CO$ show that the original cyclopentadiene-ring protons at 4.14 ppm shift to pyrylium-ring protons [7] at 9.96 ppm for **1** and at 9.89 ppm for **2**, respectively. The chemical shifts of pyrylium-ring in the ^{13}C NMR spectrum were 209.97, 206.20, 173.61, 170.55 and 164.03 ppm. The mass spectra of **1** and **2** prove the existence of the intact cation at *m*/*z* 385 ($Ph_4HC_5O^+$).

The UV–Vis absorption spectra of the two compounds show completely different absorption features from their precursor ligand $Ph_4H_2C_5$. It is observed from Fig. 1 that the precursor ligand $Ph_4H_2C_5$ exhibits a strong absorption band around 350 nm, which may be attributable to the intramolecular charge-transfer [17]. In contrast, complex **1** and/or **2** did not give such absorption band, but tailed off into the visible region. This could probably be interpreted as the effect of coordinated Ag(I) ion, which changed the π-delocalization length [17c].

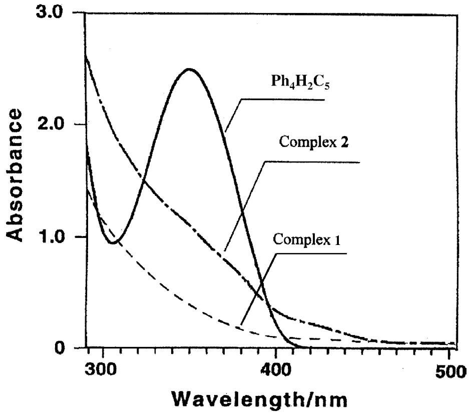


Fig. 1. UV–Vis spectra of complexes **1**, **2** and their precursor ligand in toluene.

3.2. Description of the structures

3.2.1. $(Ph_4HC_5O^+)[Ag(ClO_4)_2]^-$ (1)

The molecular structure of complex **1** together with atom-numbering scheme is shown in Fig. 2(a). The crystallographic studies revealed that the original central five-membered ring of precursor ligand $Ph_4H_2C_5$ was converted to a six-membered ring by insertion of an oxygen atom. The O atom and the five C atoms in the newly formed central ring are coplanar, with maximum deviation from the best plane being less than 0.025 Å. Such rings are iso-electronic with benzene and therefore show aromatic character [17,18]. The C–C and C–O bond lengths together with the bond angles in the central ring range from 1.319(6) to 1.416(7) Å and 118.1(4) to 122.1(4)°, respectively, within the limits from 1.254(8) to 1.538(8) Å and 108.6(5)° to 125.8(6)° in documented pyrylium cations [19]. The coordination geometry around silver(I) ion is pseudo-tetrahedral (taking the C=C group as one ligand) [9,10], comprising two oxygen atoms from two separate perchlorate anions and two η^2-carbon atoms from two neighboring phenyl rings. The Ag–C distances range from 2.523(7) to 2.774(8) Å. The next closest contact between silver and carbon atoms is 2.948(6) Å, well beyond the limits observed in the reported silver(I)–aromatic complexes [9,10,20]. The two Ag–O distances are 2.317(7) and 2.404(6) Å, respectively. The overall structure thus formed is a discrete mononuclear complex. The positively charged central pyrylium ring exhibits a neutral feature in its solid state by the static interaction with a neighboring perchlorate anion shown in its cell packing, Fig. 2(b).

3.2.2. $[Ag(ClO_4)(H_2O)(Ph_4HC_5O^+)](ClO_4^-)$ (2)

By using water-adsorbed precursor ligand $Ph_4H_2C_5 \cdot nH_2O$ in place of $Ph_4H_2C_5$ in the above reaction, a changed coordination framework, complex **2**, was isolated, whose molecular structure is given in Fig. 3(a). Complex **2** also involves a central six-membered

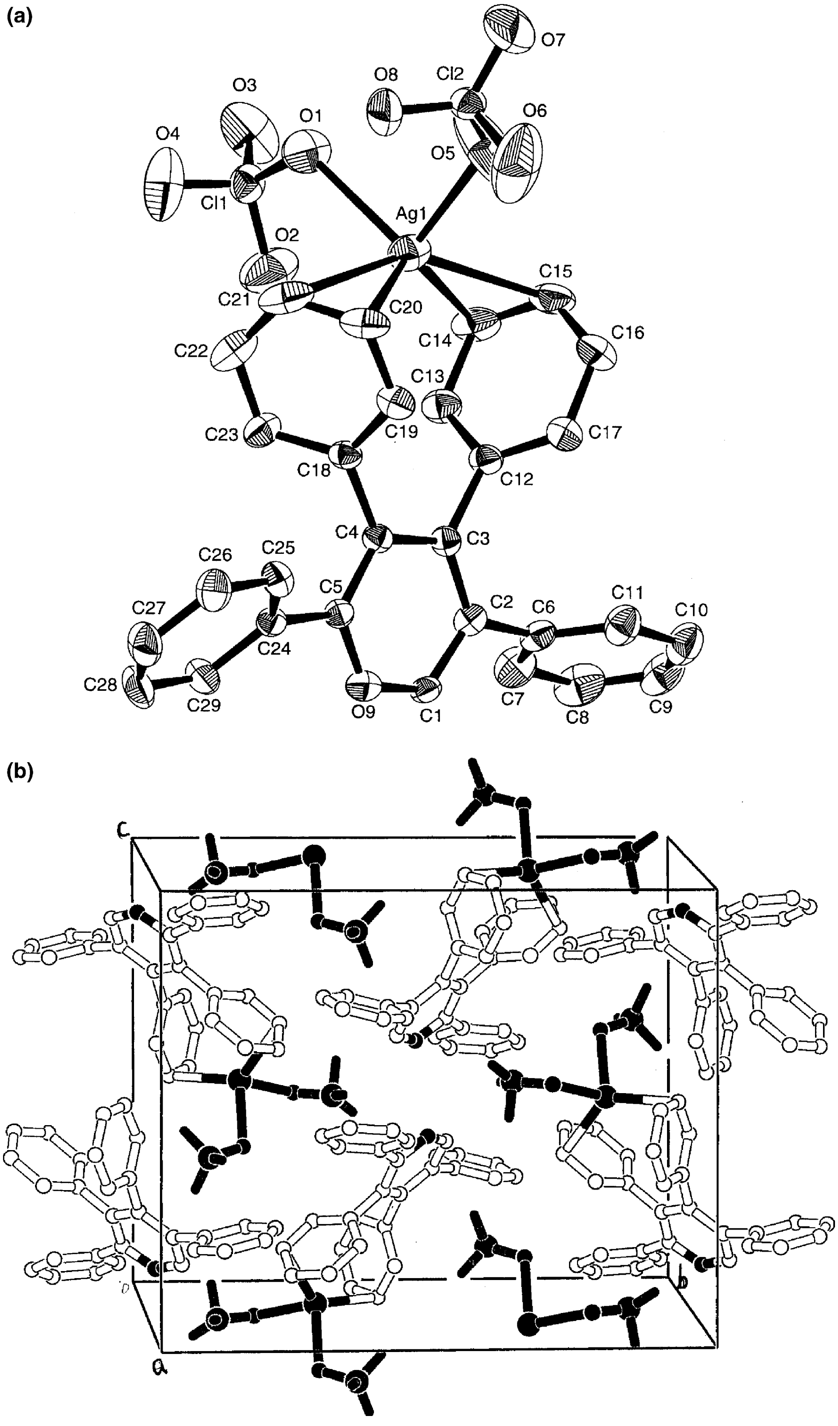


Fig. 2. Crystal structure with labeling of pyrylium cations in **1** (a), cell packing of **1** (b).

pyrylium ring. The C–C and C–O bond lengths of the pyrylium ring range from 1.33(1) to 1.40(1) Å, and their bond angles are from 117.3(9)° to 123.3(8)°. The six atoms in the pyrylium ring present the same coplanar feature as those in **1**. Furthermore, the silver(I) ion is bonded by the same couple of phenyl rings as that in **1**. However, unlike **1** where the metal ion exhibits a distorted tetrahedral geometry, silver(I) ion in **2** displays a three-coordinate environment (taking the C=C group as one ligand) [9,10]. Apart from the two bridging bonds from the couple of phenyl rings, its third coordination site is occupied by one oxygen atom from water, leaving two perchlorate anions free from coordination. The bond distances of Ag–C range from 2.53(1) to 2.677(10) Å, and Ag–O is 2.243(7) Å. The next closest Ag–C and Ag–O distances are larger than 3.6 and

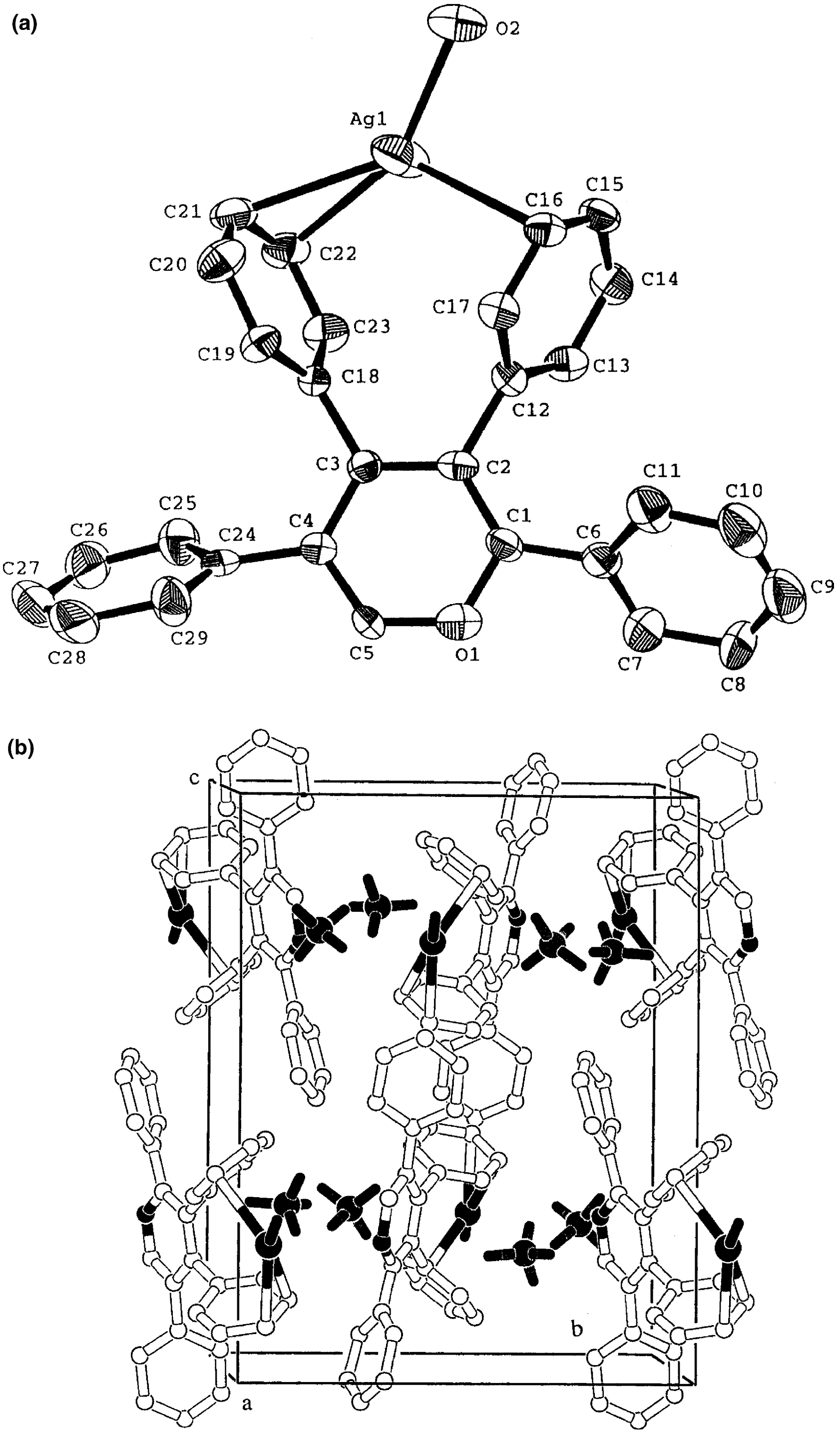


Fig. 3. Crystal structure with labeling of pyrylium cations in **2** (a), cell packing of **2** (b).

2.762(9) Å, respectively, which can be hardly considered as an effective interaction [10]. The tetraphenyl-pyrylium cation interacts with silver(I) ion in an η^1/η^2 fashion, making the metal center in the cleft between the two phenyl rings. The silver(I) bridged tetraphenyl-pyrylium moiety thus formed is a double-charged cation. These cations keep neutral feature in the solid state by incorporating perchlorate anions between the pyrylium rings in their cell packing shown in Fig. 3(b).

3.3. Modification of tetra-phenyl-cyclopentadiene ligand

Our frequent experiments have proved that $Ph_nH_{6-n}C_5$ ($n = 2$–5) did not form coordination complexes with silver(I) ion in any normal solvents, although Ph_6C_6 [9] and some phenylated alkenes [21] displayed a strong coordination ability to the metal ion. This implies that the central cyclopentadiene ring (C_5) of $Ph_nH_{6-n}C_5$ ligands may dramatically affect the interaction between its peripheral phenyl rings and metal ions. Surprisingly, water molecules provide an opportunity to change the ligand structure. It has been proved by our extensive studies that the adsorbed water molecules contribute to the formation of pyrylium ring by providing inserted oxygen atom under the catalysis and oxidation of silver(I) ion [11]. The water molecule is added to the double bond of five-membered cyclopentadiene-ring in a similar way to the strained ring system [22] by a diene addition reaction [23]. Then, the formed adduct undergoes a rearrangement process giving a six-membered neutral intermediate. According to the literature [7], this intermediate is oxidized by silver(I) ion to generate the six-membered pyrylium ring. Apart from the verified pyrylium cation and silver(I) bridged complex structures described above, the increased H^+ concentration and reduced silver metal in Scheme 1 are also identified [11]. [3]

3.4. Construction of a silver(I)-pyrylium complexes

Probably due to the conjugated aromatic pyrylium ring [7] which changed the steric configuration of the original ligand, a pair of phenyl rings of the pyrylium cation become vulnerable to the silver(I) attacking. Thus, two η^2–π orbitals from the phenyl groups of tetra-phenyl pyrylium cation were bridged to a silver(I) ion, forming a silver(I)-pyrylium complex. Nevertheless, the positions of phenyl groups on the pyrylium ring may dramatically affect the coordination behavior. Of all these phenylate pyrylium salts synthesized, including bi-, tri-, tetra- and penta-phenyl ones, only tetra-phenyl pyrylium salt has proved to form coordination complex with silver(I) perchlorate. Significantly, by changing the reaction conditions such as the concentration of the reactants, solvent, and ratios of silver(I) perchlorate to precursor ligand, we cannot remove the bridged silver(I) ions from **1** and **2**, and cannot make the other phenylate pyrylium cations coordinated by silver(I), either. This may possibly be due to the proper orientations of the adjacent phenyl rings, which provide a favorable dihedral angle for silver(I) ion to incorporate [9].

On the other hand, water molecules can make the coordination frameworks dramatically modified. In complex **1**, where $Ph_4H_2C_5$ was partially dried, the η^2–π bridged silver(I) ion is connected to two oxygen atoms from two perchlorate anions to acquire a usual distorted tetrahedral coordination geometry, whereas in **2**, the increased moisture-content of $Ph_4H_2C_5$ leads to a three-coordinate metal center. This implies that water molecule plays a key role in controlling the architecture of silver(I) bridged pyrylium complexes, probably due to the much stronger interacting ability of water molecule with silver(I) ion. It can be seen from Table 2 that the Ag–C bond distances in **1** and **2** are all in normal ranges, being hardly to identify the obvious differences (taking the C=C group as one ligand) [9,10,24]. However, the Ag–O bond distances are quite different. In complex **1**, each silver(I) ion links two perchlorate anions with Ag–O distances of 2.404(6) and 2.317(7) Å, respectively, whereas in **2** the silver(I) ion is bound to one oxygen from water at a distance of 2.243(7) Å. Such a short Ag–O distance, to the best of our knowledge, has not been described in the aromatic hydrocarbon system. There is only one report describing a silver(I) bridged coordination polymer, where a water molecule is bound to a tetrahedral silver(I) ion with Ag–O distance of 2.27(3) Å [24]. In the present paper, the strongly bridged water molecule makes the two perchlorate counter-ions far from silver(I) ion, leading to a changed coordinate framework. As a consequence, the bond lengths in the pyrylium ring of **1** and **2** are different. The C–O and C–C bond lengths in **1** range from 1.319 to 1.416 Å, while those in **2** are from 1.33 to 1.40 Å. Complex **2** is unusual in the sense that the un-bridged perchlorate anion from silver(I) ion has not been observed in the silver(I) complexes with polycyclic hydrocarbon ligand, although various coordination modes of perchlorate ion have been described in the literature [9,10,24,25].

Perhaps the most striking feature of this study is the construction of silver(I) bridged tetra-phenyl-pyrylium cation from tetraphenyl-cyclopentadiene. As seen in the literature [3,7,8], a variety of substituted pyrylium cations/salts have been synthesized and characterized. However, very few studies concern organometallic substituents [8]. The silver(I)-bridged poly-phenyl-pyrylium cation, to the best of our knowledge, has not been reported before. Apart from the mild reaction conditions and easy access of some precursors, the reaction pathways and its rationalization could be of broad interest to chemists.

4. Conclusion

This study exemplifies two unprecedented silver(I) bridged pyrylium complexes from tetra-phenyl cyclopentadiene. In the presence of silver(I) ion and trace amount of water, phenylated cyclopentadienes undergo an oxidation and ring-enlargement reaction to form phenylated pyrylium ligands. The coordination of silver(I) ion to the phenylated pyrylium group occurs only when 1,2,3,4-tetraphenyl cyclopentadiene was selected as precursor ligand. The coordination pattern of the complexes is dependent on the moisture-content of the precursor li-

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[3] The H^+ concentration was measured with pH meter in aqueous solution by extracting the protic acid into water. Silver metal was detected using XRD spectrometer.

gand. With the increase of water adsorbed in $Ph_4H_2C_5$, the metal center in the pyrylium complexes changes from distorted tetrahedral geometry to three-coordinate environment. The results obtained here open an avenue to future rational design of many other metallic pyrylium compounds from cyclopentadiene derivatives.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.ica.2005.01.009.

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