Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Research paper

Halides of macrocyclic silver(II) complexes: Crystal structures with hydrogen bond network and reaction kinetics of the decomposition

Akinori Honda^{a,*}, Shunta Kakihara^a, Shuhei Ichimura^a, Kazuaki Tomono^b, Mina Matsushita^a, Rie Yamamoto^a, Emi Kikuta^a, Yoshinori Tamaki^a, Kazuo Miyamura^{a,*}

^a Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
^b Applied Chemistry Course, Faculty of Science and Engineering, Kanto-gakuin University, 1-50-1 Mutsuura Higashi Kanazawa-ku, Yokohama City, Kanagawa 236-0037, Japan

ARTICLE INFO

Keywords: Silver(II) Tetraaza macrocycle Crystal structure Spectroscopic analysis Coordination chemistry

ABSTRACT

A series of silver(II) complexes of 5*RS*,12*SR*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L) have been synthesized and characterized by X-ray crystallographic analysis and UV–vis absorption spectra. The crystal structure of [AgL(ClO₄)₂] (1), [AgL(NO₃)₂]-CH₃OH (2), [AgL(H₂O)₂]Cl₂ (3), and [AgL(H₂O)₂]Br₂ (4) showed the macrocyclic ligand L to be in the stable *trans*-III structure with *C*-methyl groups at equatorial positions. To our knowledge, this is the first report on the single crystal X-ray structural analysis of halides of silver(II) complex. Usually, silver ions form insoluble inorganic halides, but the stabilization of divalent silver ion by L, enabled characterization of the complex both in the solutions and in crystals. UV–vis analysis revealed that all complexes were in the form of $[AgL(H_2O)_2]^{2+}$ in aqueous solution. These complexes in aqueous solution were found to decompose gradually and lose orange color. The decomposition rate constants of these complexes were evaluated as 0.1012, 0.0971, 0.0981, and 0.2104 h⁻¹ for complexes 1–4, respectively. The decomposition was accelerated by Br⁻ and I⁻ anions.

1. Introduction

Transition-metal complexes with synthetic macrocyclic ligands have been of great interest in recent years [1–5]. There are numerous reports concerned with the coordination chemistry of substituted derivative of tetraazamacrocycles, such as the 14-membered cyclam (1,4,8,11-tetraazacyclotetradecane) [6–11]. These macrocyclic ligands provide ideal coordination sites and form stable complexes with various metal ions. In addition, high oxidation states such as copper(III) [12], gold(III) [13], ruthenium(IV) [14] are reported to exist more stably by the macrocyclic effect.

One example of stabilization of unusual oxidation states with macrocyclic ligands is found with silver(II) [15]. Di- and trivalent silver ions are rather unstable due to the powerful oxidizing nature of these ions in solution. Although the kinetics and mechanism of the oxidation of 2-mercaptopyrimidine by square planar macrocyclic tetraaza silver (II) complex as an oxidizing agent have been reported [16], the chemistry of silver(II) complex of cyclam is still under investigation. Among such investigations, an interesting reaction, disproportionation occurs

when silver(I) salts are mixed with the macrocyclic amines (L) [17].

$2 \ Ag(I) + L \leftrightarrow AgL(II) + Ag(0)$

This process occurs when the "bonding cavity" available for a metal ion in the ligand molecule is large enough for the incorporation of Ag(II), but too small to form a complex with four Ag(I)–N bonds [18]. In fact, Ag (I) ion tends to form linear di-coordinated complex. Clarck and Harrowfield [19] have examined the disproportionation behavior and concluded that it is irreversible in acetone and methanol, irreversible to a great extent in DMF, and practically absent in DMSO and acetonitrile. This silver(II) complex was isolated and crystallized as [Ag(cyclam) (ClO₄)₂] [20], [Ag(tmc)(ClO₄)₂] (tmc = 1,4,8,11-tetramethyl-1,4,8,11tetraazacyclotetradecane; *N*-tetramethyl-cyclam) [21], [Ag(tet *b*) (ClO₄)₂] (tet *b* = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) [22]. These complexes are exceptionally stable compared to silver(II) complexes with nitrogen heterocycles and related ligands, which are often quite stable in the solid state, but in solution they are powerful oxidants with little stability.

Most of the reported silver(II) macrocyclic complex salts have

* Corresponding authors. *E-mail addresses:* honda-akinori@rs.tus.ac.jp (A. Honda), miyamura@rs.kagu.tus.ac.jp (K. Miyamura).

https://doi.org/10.1016/j.ica.2021.120431

Received 17 March 2021; Received in revised form 26 April 2021; Accepted 26 April 2021 Available online 30 April 2021 0020-1693/© 2021 Elsevier B.V. All rights reserved.



perchlorate as counter anion. Conversely, the complex salts with halides are hardly formed. Halides are known to react strongly with silver(I), therefore, silver ions are usually omitted from the complex forming reaction due to the disproportionation. In this paper, we report the synthesis of four silver(II) (5RS,12SR-1,5,8,12-tetramethyl-1,4,8,11tetraazacyclotetradecane; L) complex salts with various counter anions, including halides (ClO_4^- , NO_3^- , Cl^- and Br^-). Furthermore, we investigated the characteristic of these complex salts in crystal structure and the influence of counter anions on decomposition reaction in aqueous solution. We have reported the synthesis of L and its nickel(II) complex by non-template reaction [23]. Additionally, L has two *C*-methyl groups and two *N*-methyl groups so that this ligand L can be regarded as an intermediate of cyclam (no *N*-methyl) and tmc (four *N*-methyl groups). Therefore, the variations in structural and spectral data depending on the central metal ions or ligands were investigated.

2. Experimental

All chemicals were of reagent grade and used without further purification. Macrocyclic tetramine L and its precursor, diaminodi-imine L' (L' = 1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetrdeca-4,11-diene) were synthesized according to the literature, and used as ligands [24]. Perchlorates are potentially explosive in general, and the experiments should be conducted in a small scale.

2.1. Reagents and chemicals

2.1.1. (5RS,12SR-1,5,8,12-tetramethyl-1,4,8,11-

tetraazacyclotetradecane)silver(II) diperchlorate [AgL(ClO₄)₂] (1)

Silver(I) perchlorate (1.617 g, 7.8 mmol) and ligand L (0.974 g, 3.8 mmol) were stirred in water (10 mL) for 2–3 h. Silver metal gradually deposited on flask surface and at the same time the solution changed into orange color. This mixture **1** was filtered in order to remove the precipitated metallic silver and the filtrate was cooled in a refrigerator. The orange precipitates thus formed were collected by filtration. The crude product of **1** was purified by recrystallization from acetonitrile and ethanol to give crystal suitable for X-ray crystallographic analysis. Yields: 0.182 g, 8.5%. Calc. for C₁₄H₃₂AgCl₂N₄O₈: C, 29.86; H, 5.73; N, 9.95%. Found: C, 30.01; H, 5.64; N, 9.89%. IR spectrum (KBr pellet, cm⁻¹): 3236 (N–H, *s*), 2979 (*w*), 2818 (*w*), 1467 (*m*), 1417 (*m*), 1086 (*s*), 625 (*s*). UV–vis measurement: $\lambda_{max}/nm 354$ ($\varepsilon/L mol^{-1} cm^{-1} 1.04 \times 10^4$).

2.1.2. (5RS, 12SR-1, 5, 8, 12-tetramethyl-1, 4, 8, 11-

tetraazacyclotetradecane)silver(II) dinitrate methanol monosolvate [AgL (NO₃)₂]-CH₃OH (**2**)

Silver(I) nitrate (1.308 g, 7.7 mmol) and ligand L (0.974 g, 3.8 mmol) were stirred in water (10 mL) for 2–3 h. This mixture was filtered in order to remove the precipitated metallic silver, and the solvent of filtrate was removed under reduced pressure. The crude orange precipitate of **2** was purified by recrystallization from hot methanol and to give crystal suitable for X-ray crystallographic analysis. Yields: 0.154 g 7.8%. Calc. for C₁₅H₃₆AgN₆O₇: C, 34.62; H, 6.97; N, 16.15%. Found: C, 34.92; H, 6.77; N, 16.13%. IR spectrum (KBr pellet, cm⁻¹): 3447 (O–H, *s*), 3128 (N–H, *s*), 2973 (*s*), 2874 (*w*), 2372 (*w*), 1749 (*w*), 1630 (*s*), 1459 (*s*). UV–vis measurement: λ_{max}/nm 354 (ε/L mol⁻¹ cm⁻¹ 8.04 × 10³).

2.1.3. Diaqua(5RS,12SR-1,5,8,12-tetramethyl-1,4,8,11-

tetraazacyclotetradecane)silver(II) dichloride [AgL(H₂O)₂]Cl₂ (3)

Orange complex salt **3** was obtained by the exchanging counter anion of **1**. Counter anion was exchanged from perchlorate to chloride ion by anion-exchange resin (AG3-X4A). Crude yield was 5.2% for complexes **3**. As noted below, single crystals of **3** and **4** for X-ray analysis were difficult to be recrystallized because of the degradation of complexes ending up with silver deposition. The single crystals suitable for X-ray diffraction were obtained by slow-evaporation method of aqueous solution. Calc. for $C_{14}H_{36}AgCl_2N_4O_2$: C, 35.68; H, 7.70; N, 11.89%. Found: C, 35.59; H, 7.65; N, 11.56%. IR spectrum (KBr pellet, cm⁻¹): 3419 (O—H, *s*), 3089 (N—H, *s*), 2962, 2888, 1461 (*s*), 1419 (*s*), 1112 (*s*), 1028 (*s*), 762 (*m*). UV–vis measurement: λ_{max} /nm 354 (ε /L mol⁻¹ cm⁻¹ 9.12 × 10³).

2.1.4. Diaqua(5RS,12SR-1,5,8,12-tetramethyl-1,4,8,11-

tetraazacyclotetradecane)silver(II) dibromide $[AgL(H_2O)_2]Br_2$ (4)

Complex **4** was synthesized by a similar procedure to **3** using bromide form of AG3-X4A. Crude yield was 4.7% for complexes **4**. Calc. for C₁₄H₃₆AgBr₂N₄O₂: C, 30.02; H, 6.48; N, 10.00%. Found: C, 30.06; H, 6.56; N, 10.27%. IR spectrum (KBr pellet, cm⁻¹): 3389 (O—H, *s*), 3101 (N—H, s), 2963 (*m*), 2875 (*m*), 1459 (*m*), 1419 (*m*), 1110 (*m*), 1024 (*m*), 763 (*w*). UV–vis measurement: λ_{max} /nm 354 (ε /L mol⁻¹ cm⁻¹ 8.37 × 10³).

2.2. Measurement

IR spectra were measured with a JASCO FT/IR-410 spectrophotometer. Elemental analyses were performed by a Perkin-Elmer 2400II Analyzer. UV–vis-NIR spectra were recorded with a JASCO V-570 UV/VIS/NIR spectrophotometer, with sample concentration of 1.0×10^{-4} mol L⁻¹ (aqueous solution). In the case of **3** and **4**, single crystal suitable for X-ray analysis could only be obtained by first crystallization. Usual re-crystallization procedure led to partial decomposition of Ag(II) complex.

2.3. X-ray crystallography

Single crystal was mounted on a glass capillary. Intensity data were collected by a Bruker AXS SMART diffractometer equipped with CCD area detector and MoK α ($\lambda = 0.71073$ Å) radiation. The structures of 1–4 were solved and refined with the SHELX-97 [25] and SHELXL-2016 [26] using direct method and expanded using Fourier techniques. All nonhydrogen atoms were refined anisotropically by the full-matrix leastsquare method. Hydrogen atoms bound to oxygen or nitrogen atoms were found in a difference Fourier map, and their position and isotropic thermal parameters were refined. All H atoms bound to carbon atoms were placed at idealized positions and refined using a riding model. Selected crystallographic data are summarized in Table 1. Crystallographic data have been deposited on Cambridge Crystallographic Data Centre: Deposit numbers CCDC-763972-763975 for compounds 1-4, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; FAX: +44 1223 336033; mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Synthesis and structural analysis

In our previous paper [23], we have reported convenient and selective synthetic paths to obtain isomers of nickel(II) complex of **L** with either *C*-equatorial and *C*-axial configurations. By the reduction of diamino-di-imine after complexation led to *C*-equatorial isomer, while reducing diamino-di-imine ligand before complexation gave *C*-axial isomer. According to our papers [23,24,27], nickel(II) complex of **L** with *C*-equatorial configuration adopted six-coordinated octahedral geometry with two water molecules occupying two apical sites, while the apical sites of nickel(II) complex of **L** with *C*-axial configuration were vacant resulting in four coordinate square-planar geometry. Furthermore, copper(II) complex of **L** with *C*-axial configuration adopted five coordinated square-pyramidal geometry with one water molecule occupying one of two apical sites. In the silver complexes, only *C*equatorial isomer was obtained even the complexation was carried out

Table 1

Crystallographic data for 1–4.

	Complexes				
	1	2	3	4	
Formula	C14H32AgCl2N4O8	$C_{15}H_{36}AgN_6O_7$	$C_{14}H_{36}AgCl_2N_4O_2$	$C_{14}H_{36}AgBr_2N_4O_2$	
Formula weight	563.21	520.37	471.24	560.16	
Crystal Size (mm)	0.14 imes 0.13 imes 0.10	$0.40\times0.25\times0.10$	0.11 imes 0.11 imes 0.07	0.25 imes 0.24 imes 0.12	
Temperature (K)	297(1)	297(1)	297(1)	297(1)	
Crystal System	Triclinic	Monoclinic	Monoclinic	Monoclinic	
Space Group	P-1	P2(1)/n	P2(1)/n	P2(1)/n	
a (Å)	8.326(2)	11.127(2)	9.1318(13)	9.3559(8)	
b (Å)	8.725(2)	15.175(3)	11.8882(16)	12.1708(11)	
c (Å)	8.796(2)	13.013(2)	9.6286(13)	9.7373(9)	
α (°)	76.118(4)				
β(°)	70.144(4)	94.159(2)	107.454(2)	107.7800(10)	
γ (°)	69.486(4)				
Volume (Å ³)	557.6(2)	2191.5(7)	997.2(2)	1055.82(16)	
Ζ	1	4	2	2	
$D_c ({\rm Mg}/{\rm m}^{-3})$	1.677	1.577	1.569	1.762	
$\mu (mm^{-1})$	1.190	0.967	1.292	4.752	
GOF	1.171	1.042	0.989	0.959	
R1	0.0527	0.0570	0.0353	0.0239	
wR2	0.1483	0.1475	0.0841	0.0543	

after the reduction. The obtained silver complexes were relatively stable in the solid state.

Fig. 1 shows the ORTEP [28] drawings with atom numbering scheme of 1–4. These structures included solvent molecules except for 1. The complex salt with I^- was not obtained because formulation of AgI is faster than stabilization of complex salt. Macrocyclic tetramine L coordinated to silver(II) as a quadridentate ligand, and its four nitrogen-

donor atoms occupied the planar coordination sites. The configuration of the cyclam moiety of L was stable *trans*-III where all four chelate rings were in the stable skew (five-membered ring) or chair (six-membered ring) conformations. Note that two *C*-methyl groups adopted equatorial configuration and two *N*-methyl groups adopted axial configuration. Silver(II) ion was coordinated by four nitrogen atoms of L, and two molecules occupied the apical sites to adopt six coordinated distorted



Fig. 1. ORTEP views of (a) 1, (b) 2, (c) 3, and (d) 4 showing 30% probability ellipsoids with atom numbering scheme. H atoms were omitted for clarity.

octahedral geometry as a whole. Selected bond lengths and bond angles are listed in Table 2. The bond length Ag–O in 1 was shorter than that in the complexes 2–4. Ag–N(1) (N(1) = secondary amino groups) bond length tended to be shorter than Ag–N(2) (N(2) = tertiary amino groups) in all complex (1–4).

In complex 1, silver atom on the inversion center was coordinated by four nitrogen atoms of L in planar form, and two perchlorate ions were weakly coordinated to two apical sites. The crystal packing is shown in Fig. 2a. Amine hydrogen atoms are found to form hydrogen bond with perchlorate ions, as shown in Fig. 3a, and related parameters are tabulated in Table 3. N-H--O hydrogen bonds and O-Ag-O bonds linked the Ag(II) complexes in 1-D strand (see Figs. 3a and 2a). The average of Ag–N bond lengths was 2.161(3) Å, which was in good agreement but was almost intermediate to the average values of 2.158(2) Å in [Ag(II) (cyclam)](ClO₄)₂ [20] and 2.195(3) Å in [Ag(II)(tmc)](ClO₄)₂ [21]. Substitution by *N*-methyl group seemed to elongate the Ag–N distance. Ag–O(1) bond length 2.728(5) Å for coordinated perchlorate ion was slightly shorter than the corresponding distances in [Ag(cyclam) (ClO₄)₂] 2.788(2) Å [20] and [Ag(tmc)(ClO₄)₂] 2.889(4) Å [21], indicating stronger coordination of perchlorate in complex ${\bf 1}$ than that in other complexes.

In complex **2**, on the other hand, the asymmetric unit contained one crystallographically independent $[AgL]^{2+}$ cation, two nitrate anions and one methanol as crystal solvent. X-ray analysis has revealed that the crystal structure of **2** consists of 1-D zigzag chains (see Fig. 2b) of $[AgL]^{2+}$ bridged by one of the two NO₃⁻. Ag(II) ion was six-coordinate,

Table 2

Selected bond lengths [Å] and angles [°].

$[AgL(ClO_4)_2] (1)$					
Bond lengths					
Ag1–N1	2.138(5)	Ag1–N2	2.182(5)		
Ag1–O1	2.728(5)				
Bond angles					
N1–Ag1–N2	94.3(2)	N1–Ag1–N2 ⁱ	85.7(2)		
Ag1–N2–C5	115.8(4)	N1-Ag1-O1	84.5(2)		
N2–Ag1–O1	91.9(2)				
[AgL(NO ₃) ₂]·CH ₃ OH (2	2)				
Bond lengths					
Ag1–N1	2.162(4)	Ag1–N2	2.168(3)		
Ag1–N3	2.166(4)	Ag1–N4	2.169(3)		
Ag1-01	2.917(5)	Ag1–O3 ⁱⁱ	2.964(4)		
Bond angles					
N1–Ag1–N2	95.06(15)	N2–Ag1–N3	85.35(14)		
Ag1–N2–C5	114.7(3)	N1-Ag1-O1	98.16(17)		
N2-Ag1-O1	90.06(14)				
[AgL(H ₂ O) ₂]Cl ₂ (3)					
Bond lengths					
Ag1–N1	2.164(3)	Ag1–N2	2.181(3)		
Ag1-01	2.938(3)	0			
-					
Bond angles					
N1–Ag1–N2	95.14(10)	N1–Ag1–N2 ⁱⁱⁱ	84.86(10)		
Ag1–N2–C5	114.9 (2)	N1-Ag1-O1	90.76(10)		
N2–Ag1–O1	94.50(10)				
$[AgL(H_2O)_2]Br_2$ (4)					
Bond lengths					
Ag1-N1	2,159(2)	Ag1-N2	2,184(17)		
Ag1-01	2.984(2)		,		
Bond angles					
N1-Ag1-N2	95.52(7)	N1–Ag1–N2 ^{iv}	84.48(7)		
Ag1–N2–C5	114.40(14)	N1–Ag1–O1	89.83(7)		
N2-Ag1-O1	95.70(7)				

Symmetry codes: (i) –x, 2 – y, 1 – z; (ii) 3/2 - x, -1/2 + y, 3/2 - z; (iii) 1 – x, 1 – y, 1 – z; (iv) 1 – x, 1 – y, 1 – z.



Fig. 2. Crystal structures of (a) 1 and (b) 2. The dashed lines indicate weak coordination of apical ligands to silver. All H atoms are omitted for clarity.



Fig. 3. Hydrogen bonded network of (a) 1 and (b) 2 between complexes and counter anions (ClO_4^- or non-coordinated NO_3^-). The dashed lines indicate $N\cdots O$ hydrogen bonds.

Table 3

Hydrogen bonding parameters for $[AgL(ClO_4)_2]$ (1), $[AgL(NO_3)_2] \cdot CH_3OH$ (2), $[AgL(H_2O)_2]Cl_2$ (3), and $[AgL(H_2O)_2]Br_2$ (4).

	D–H···A	H…A [Å]	D…A [Å]	D–H…A [°]
1	$N1-H1\cdots O2^{i}$	2.56(8)	3.209(8)	134
	$N1-H1\cdots O4^{i}$	2.37(8)	3.168(9)	158
2	N1-H1····O4 ⁱⁱ	2.13(5)	2.863(6)	150
	N3-H3-···O5	2.42(5)	3.261(7)	164
	N3-H3-···O6	2.33(5)	3.010(6)	136
	07-H701	2.41(3)	3.175(9)	155
	07–H7…O3	2.30(3)	3.038(8)	150
3	N1-H1Cl1	2.29	3.265(3)	177
	O1-H2…Cl1	2.41(3)	3.182(3)	160
	O1–H3…Cl1 ⁱⁱⁱ	2.41(2)	3.222(4)	165
4	N1–H1…Br1	2.43	3.411(19)	177
	O1-H2…Br1	2.51(2)	3.292(3)	157
	O1–H3…Br1 ^{iv}	2.49(19)	3.331(3)	173

Symmetry codes: [i] 1 - x, 2 - y, 1 - z; [ii] 3/2 - x, 1/2 + y, 3/2 - z; [iii] -1/2 + x, 3/2 - y, -1/2 + z; [iv] 1/2 + x, 3/2 - y, 1/2 + z.

complexed with four nitrogen atoms of **L** and two different oxygen atoms (O(1) and O(3)) of nitrate anions at two apical positions. Four Ag–N bond lengths of **2** were almost the same distance in the range of 2.162–2.169 Å. Ag–N(1) bond length tended to be shorter than Ag–N(2) in all complex (**1**–**4**). However, the elongation by *N*-methyl substitution in **2** was small compared with other salts. In this crystal, one of the two nitrate anions was not coordinated directly to Ag(II). The closest distance between oxygen atom (O(5)) of non-coordinated nitrate and silver

was 4.394 Å. Three N—H…O hydrogen bonds between amino hydrogen of L and non-coordinated nitrate ion evidenced by IR spectra were observed (Fig. 3b). For 2, v(N-H) appeared at about 3128 cm⁻¹, which was about 100 cm⁻¹ lower than 3236 cm⁻¹ observed for **1**. Additionally, O-H--O hydrogen bonds were observed between non-coordinate nitrate and methanol of crystal solvent. Thus, we concluded that the small deviation of Ag-N bond lengths in 2 was brought about by the presence of the three strong hydrogen bond networks between silver complex and counter anion or the effect of packing structure including the hydrogen bond networks. In contrast, Ag-O bond lengths 2.917(5) and 2.964(4) Å for coordinated nitrate ions were much longer than 1. In the case of 2, apical sites NO3 were also stabilized by hydrogen bond between methanol and NO₃⁻, causing the longer Ag–O length. In fact, the corresponding distance in [Ag(tet a)(NO₃)₂] (tet a = meso-5,5,7,12,12,14hexamethyl-1,4,8,11-tetraazacyclotetradecane) [29], which is not include crystal solvent, is 2.807(4) Å, shorter than that in 2.

Crystals of 3 and 4 were found to be almost isomorphous. Silver(II) ion was surrounded by four nitrogen atoms of L and two oxygen atoms of the two water molecules to adopt six-coordinated octahedral geometry as a whole. Furthermore, Jahn-Teller distortion due to the weak coordination to axial position, a characteristic of d⁹ system, was observed. Ag–O(1) bond length (2.938(3) Å in chloride salt (3) and 2.984(2) Å in bromide one (4)) for coordinated water molecules were shorter than 3.24 Å, the sum of van der Waals radii. It was interesting to note that there were no particular interactions between silver and halide ions. The closest distances between silver and halide ions were 4.379 Å in chloride salt and 4.500 Å in bromide one. Similar situation was reported in [Ag₂(TSCZ)₆]Cl₂ [TSCZ = thiosemicarbazide; SC(NH₂)NHNH₂] complex where silver ion was monovalent [30]. In [Ag₂(TSCZ)₆]Cl₂, Cl⁻ ion did not interact directly with the central silver but rather formed N-H···Cl hydrogen bonds with TSCZ ligands [30]. Apical coordination of water molecule was weak in 3, and the Ag-O bond distances were clearly longer than those of the perchlorate ion (2.728(5) Å) in 1. As shown in our previous report [23,24,27], the use of nickel(II) as central metal ion resulted in opposite result. The Ni-O bond length of chloride salt (2.210 Å) [24] was shorter than that of perchlorate salt (2.887 Å) [23]. However, in the case of copper(II) complexes, Cu–O bond length of chloride salt (2.692 Å) [27] was almost the same to that of the perchlorate salt (2.696 Å) [31].

Regarding the intermolecular interaction, two complexes **3** and **4** together with halide ions (Cl⁻ or Br⁻) and water were found to construct a network of hydrogen bonds. The crystal packing and hydrogen bond network of **3** and **4** are shown in Figs. 4 and 5. Two hydrogen atoms of a water molecule were involved in hydrogen bonding, where one atom is bound to the halide ion (Cl⁻ or Br⁻), and another one to the symmetry related halide ion. Amino hydrogen atoms were also hydrogen bound to the halide ion. The parameters related to N—H…X and O—H…X (X =



Inorganica Chimica Acta 524 (2021) 120431

Cl⁻ or Br⁻) hydrogen bonds of **3** and **4** are tabulated in Table 3. The parameters of N—H···Cl hydrogen bonds were almost the same between **3**, Cu(II) ([CuL(H₂O)₂]Cl₂) [27,31], and Ni(II) ([NiL(H₂O)₂]Cl₂) [24], although the IR peak of each v(N—H) were found to be different. The v (N—H) bands in IR spectra of Ag(II), Cu(II), and Ni(II) complexes were 3089, 3090, and 3137 cm⁻¹ respectively. Conversely, both the average O···Cl distance and v(O—H) band in the IR spectra were different between [AgL(H₂O)₂]Cl₂ **3**, [CuL(H₂O)₂]Cl₂, and [NiL(H₂O)₂]Cl₂: 3.202 Å (3419 cm⁻¹), 3.174 Å (3355 cm⁻¹), and 3.188 Å (3301 cm⁻¹), respectively. These results indicate that Cl⁻ is bound strongly to N—H rather than to O—H in silver(II) complex.

3.2. UV-vis investigation

The kinetic stability of Ag(II) complex was studied in aqueous solution by monitoring the absorbance change at wavelength of 250-500 nm. UV-vis spectral change of 1 and 4 in water $(1.0 \times 10^{-4} \text{ mol L}^{-1})$ are shown in Fig. 6a and b. The spectra of 2 and 3 were similar to that of 1 (Fig. S1a and b). One strong peak at ca. 354 nm and a shoulder peak at ca. 280 nm were observed. Note that the UV-vis spectra of these complexes were almost the same at 0 h, and the absorption maxima did not depend on the counter anion. This implies that all complexes are in the form of $\left[\text{AgL}(\text{H}_2\text{O})_2\right]^{2+}$ in aqueous solution. Estimating from the value of ε (order of 10³ L mol⁻¹ cm⁻¹), the absorption peaks were assigned as CT transition. These aqueous solutions of Ag(II) complex were found to decolorate gradually. The color of the solution was yellow initially, but disappeared after a couple of days. The free Ag metals were deposited in the reaction vessel. This means that colored d⁹ Ag(II) turned into colorless d¹⁰ Ag(I) species, and then to metallic Ag(0). Macrocyclic ligand L was probably oxidized [17].

Fig. 7 shows the spectral change of complexes 1-4 at the maximum absorption wavelength (354 nm) with respect to time. The measurement was finished when the value of absorbance stopped changing. Assuming that this decay reaction is the first order reaction, the rate constant *k* is represented as follows:

$$ln\left(\frac{C}{C_0}\right) = -kt$$

where *C* is the concentration at time *t* and *C*₀ is the concentration at 0 h, and *k* is the first-order rate constant. Fig. 7 shows that **1–3** decomposes by first-order reaction but the decomposition behavior of **4** changes after 6 h. The rate constants *k* for the decay reaction at 25 °C were estimated to be 0.1012, 0.0971, and 0.0981 h⁻¹ for complexes **1–3**, respectively. Since the decomposition rate is almost the same for **1–3**, anions are not involved in the decomposition of the Ag(II) complex. However, the rate of decomposition of **4** was significantly accelerated, and the solution lost color in only 12 h. In addition, the precipitation other than black Ag(0) particles was often observed. The precipitation is considered to be AgBr. As will be described later, silver halides are very insoluble in water, owing to their lower solubility (AgCl; 1.92 × 10⁻⁴ g/100 mL and AgBr; 1.32 × 10⁻⁵ g/100 mL) than that (525 g/100 mL and 216 g/100 mL) of AgClO₄ and AgNO₃. The estimated rate constants can be correlated with the solubilities.

The reason for the remarkably fast decomposition rate of **4** can be explained as follows. First, Ag(II)L is decomposed into Ag(I) ion and L in aqueous solution by irradiation of UV–vis light in the UV–vis measurement. The ligand L may be subject to oxidation. Then, the oxidized macrocyclic ligand reacts with Ag(I) to reform Ag(II) complex together with Ag⁰ by disproportionation. In the case of **4**, AgBr easily precipitated and removed from the solution due to the low solubility to water, resulting in the decrease in Ag(I) ion and preventing the disproportionation. According to the study on the decomposition of silver halide, the stability of AgCl is lower than that of AgBr and AgI [32]. Thus, the regeneration of Ag(II) complex tends to be occurred in **3**, but depressed in **4**. UV–vis spectra of **1** with NaX (X = Cl⁻, Br⁻, I⁻) were recorded to

Fig. 4. Crystal structures of (a) 3 and (b) 4. The dashed lines indicate weak coordination of water molecules to silver at apical position. H atoms were omitted for clarity.



Fig. 5. Hydrogen bonded network of (a) **3** and (b) **4** among complexes, waters, and counter anions (Cl⁻ or Br⁻). Orange dashed lines indicate N—H…halide hydrogen bonds, and Blue ones indicate O—H…halide hydrogen bonds.



Fig. 6. Time dependent change in UV–vis spectra of (a) $[AgL(ClO_4)_2]$ (1) and (b) $[AgL(H_2O)_2]Br_2$ (4). Spectra are taken at an interval of 3 h until change in the spectra disappeared.

investigate the effect of halogens to decomposition of Ag(II)L complex (Fig. 8). The concentration of 1 and NaX was 1.0×10^{-4} mol L $^{-1}$. Decomposition rate of 1 and NaX mixed solution depended on halogens (I $^-$ > Br $^-$ > Cl $^-$). This may be relative to HSAB rule. Similarly to the case of 4, AgI can inhibit the regeneration of Ag(II)L. These results are also supported by standard oxidation-reduction potential. In the case of Br $^-$ and I $^-$, Ag(II)L gets electron from Br $_2$ or I $_2$. However, in the case of Cl $^-$, Ag(II)L receives electron from H $_2$ O because Cl $_2$ /Cl $^-$ + 1.3595 V $> O_2/$ H $_2O$ + 1.229 V. In summary, the decomposition rate depends on the stability of AgX precipitation and the concentration of Ag(I) cation and halide anion (X $^-$) in the solution.

4. Conclusion

The single crystal structures of silver(II) macrocyclic complexes were investigated. The macrocyclic ligand of [AgL(ClO₄)₂] (1), [AgL(NO₃)₂].



Fig. 7. Plots of $\ln(C/C_0)$ versus *t* taken for the decay reaction of 1–4 at 25 °C.



Fig. 8. Decomposition rate of 1 with NaX ($X = Cl^{-}, Br^{-}, I^{-}$).

CH₃OH (2), [AgL(H₂O)₂]Cl₂ (3), and [AgL(H₂O)₂]Br₂ (4) adopted the stable *trans*-III structure, and *C*-methyl groups of **L** adopted equatorial configuration. The single crystals of halides of silver(II) complex were obtained due to the stabilization by macrocyclic effect. Additionally, hydrogen bond network between the complexes and counter anions stabilized the crystal structures. In addition to the crystal structural analysis, the characteristic of the complexes in solution was investigated. The UV–vis spectra revealed that all complexes **1–4** were in the form of [AgL(H₂O)₂]²⁺ in aqueous solution, but the decomposition rate depended on the counter anions. Especially, bromide and iodide ions accelerated the decomposition owing to the lower solubility of AgBr and AgI.

CRediT authorship contribution statement

Akinori Honda: Formal analysis, Investigation, Writing - original draft, Visualization. Shunta Kakihara: Formal analysis, Investigation, Visualization. Shuhei Ichimura: Validation, Investigation. Kazuaki Tomono: Validation, Investigation. Mina Matsushita: Validation, Investigation. Rie Yamamoto: Investigation. Emi Kikuta: Investigation. Yoshinori Tamaki: Investigation. Kazuo Miyamura: Conceptualization, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120431.

References

- [1] H. Shi, J. Xie, W.W.Y. Lam, W.-L. Man, C.-K. Mak, S.-M. Yiu, H.K. Lee, T.-C. Lau, Chem. Eur. J. 25 (2019) 12895–12899.
- [2] V. Pirovano, A. Caselli, A. Colombo, C. Dragonetti, M. Giannangeli, E. Rossi, E. Brambilla, ChemCatChem 12 (2020) 5250–5255.
- [3] S. Ghosh, S. Selvamani, S. Mehta, A. Mondal, Dalton Trans. 49 (2020) 9208-9212.
- [4] N.D. Savić, B.B. Petković, S. Vojnovic, M. Mojicevic, H. Wadepohl, K. Olaifa, E. Marsili, J.N. Runic, M.I. Djuran, B.D. Glišić, Dalton Trans. 49 (2020) 10880–10894.
- [5] P.G. Barros, D. Moonshiram, M.G. Sepulcre, P. Pelosin, C.G. Suriñach, J. B. Buchholz, A. Llobet, J. Am. Chem. Soc. 142 (2020) 17434–17446.

- [6] A. Zhanaidarova, C.E. Moore, M. Gembicky, C.P. Kubiak, Chem. Commun. 54 (2018) 4116–4119.
- [7] M. Paúrová, T. David, I. Císarová, P. Lubal, P. Hermann, J. Kotek, New J. Chem. 42 (2018) (1929) 11908–11911.
- [8] T.J. Hubin, A.N. Walker, D.J. Davilla, T.N.C. Freeman, B.M. Epley, T.R. Hasley, P. N.A. Amoyaw, S. Jain, S.J. Archibald, T.J. Prior, J.A. Krause, A.G. Oliver, B. L. Tekwani, M.O.F. Khan, Polyhedron 163 (2019) 42–53.
- [9] S.F. Robey, B.L. Mash, T. Jiang, M. Zeller, T. Ren, Polyhedron 170 (2019) 471–475.
 [10] E.V. Basiuk, C.C.O. Bravo, V.G. Vidales, M. Kakazey, V.A. Basiuk, J. Mater. Sci. 55
- (2020) 5364–5377. [11] S.M. Abozeid, D. Asik, G.E. Sokolow, J.F. Lovell, A.Y. Nazarenko, J.R. Morrow,
- Angew. Chem. Int. Ed. 59 (2020) 12093–12097. [12] D.C. Olson, J. Vasilevskis, Inorg. Chem. 10 (1971) 463–470.
- [13] E. Kimura, Y. Kurogi, T. Koike, M. Shionoya, Y. Iitaka, J. Coord. Chem. 28 (1993) 33–49.
- [14] Chi-Ming Che, Kwok-Yin Wong, Chung-Kwong Poon, Inorg. Chem. 25 (1986) 1809–1813.
- [15] E.K. Barefield, M.T. Mocella, Inorg. Chem. 12 (1973) 2829-2832.
- [16] R. Trismitro, H.N. Po, J. Coord. Chem. 17 (1988) 1-14.
- [17] M.O. Kestner, A.L. Allred, J. Am. Chem. Soc. 94 (1972) 7189-7190.
- [18] B. Olejniczak, J. Dziegiee, A. Grzejdziak, Monatshefte für Chemie 128 (1997) 13–21.
- [19] I.J. Clark, J.M. Harrowfield, Inorg. Chem. 23 (1984) 3740-3745.
- [20] T. Ito, H. Ito, K. Toriumi, Chem. Lett. 10 (1981) 1101–1104.
- [21] H.N. Po, E. Brinkman, Acta Crystllogr. C 47 (1991) 2310–2312.
- [22] H.N. Po, Shu-Chin Shen, Acta Crystallogr. C 49 (1993) 1914–1916.
- [23] K. Miyamura, M. Kohzuki, R. Narushima, M. Saburi, Y. Gohshi, J. Chem. Soc., Dalton Trans. 12 (1987) 3093–3098.
- [24] H. Kawamura, K. Ono, K. Tomono, K. Miyamura, Inorg. Chim. Acta 362 (2009) 4804–4808.
- [25] G.M. Sheldrick, Acta Crystalogr., A 64 (2008) 112-122.
- [26] G.M. Sheldrick, Acta Crystallogr., C 71 (2015) 3-8.
- [27] K. Tomono, E. Otani, R. Ikwda, Y. Sonwta, N. Saita, K. Miyamura, J. Incl. Phenom. Macrocycl. Chem. 70 (2011) 241–247.
- [28] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.
- [29] K.B. Mertes, Inorg. Chem. 17 (1978) 49-52.
- [30] A.C. Bonamartini, G.F. Gasparri, M.F. Belicchi, M. Nardelli, Acta. Crystallogr. C 43 (1987) 407–413.
- [31] T. Lu, S. Lin, H. Aneetha, K. Panneerselvam, C. Chung, J. Chem. Soc., Dalton Trans. 19 (1999) 3385–3391.
- [32] D. Hayes, K.H. Schmidt, D. Meisel, J. Phys. Chem. 93 (1989) 6100-6109.