

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Decarboxylation and simultaneous reduction of silver(I) β -ketocarboxylates with three types of coordination

Mariko Hatamura^{*a}, Shunro Yamaguchi^{*a}, Shin-ya Takane^b, Yu Chen^b, and Katuaki Suganuma^a

A series of silver(I) β -ketocarboxylates were prepared by reaction of β -ketocarboxylic acids with silver nitrate in the presence of diethanolamine. The silver(I) β -ketocarboxylates decomposed over a narrow temperature range to form metallic silver, CO₂, and the corresponding ketones. In addition, products derived from radical intermediates were detected by mass spectroscopic analysis for some silver(I) β -ketocarboxylates. Infrared and solid state ¹³C-NMR spectra of silver(I) β -ketocarboxylates suggested the presence of two types of structures involving a carbonyl group in addition to the dimeric eight-membered ring structure as in the structure of silver(I) stearate. The silver(I) β -ketocarboxylate model compound used was HCOCH₂COOAg and its structures were determined using density functional theory (DFT) and atoms-in-molecules (AIM) methods. Three types of coordination around the Ag ion differing significantly in Ag-O bond strengths were found. Based on the calculated structures and experimental results, the relationship between the structures and decomposition temperatures are discussed in terms of the thermal decomposition process.

Introduction

Much attention has been paid to silver(I) carboxylates as photographic and printed electronic materials because of their unique structures and their reduction to metallic silver by thermal decomposition.¹⁻⁵ However, these silver(I) carboxylates need temperature more than 200 °C for the thermal reduction. Silver-containing materials forming metallic silver at lower temperature have been demanded in the industrial fields.

In 1949, Vand reported a preliminary structure of silver salts of fatty acids.⁶ The complete structure of silver perfluorobutyrate, composed of an eight-membered central ring containing two silver atoms and two carboxyl groups, had been elucidated.⁷ Due to the difficulty of crystallizing these salts and their light sensitivity, only a few studies describing the structure of silver carboxylates have been reported. Acland found that the silver salt of glycylglycine adopted an eight-membered ring structure about the silver carboxylate moiety.⁸ A series of crystal structures of silver carboxylate complexes containing an eight-membered ring were reported by Mak.⁹ Tolochko examined the structure of silver stearate by extended X-ray absorption fine structure (EXAFS) and reported that the Ag-Ag distance in the eight-membered ring was 2.90 Å, similar to the bond distance in metallic silver.¹⁰ Other structures of silver carboxylates that adopt an eight-membered ring have been reported,^{3,4,11-13} leading to the wide acceptance that silver carboxylates tend to form a dimeric (RCO₂)₂Ag₂ eight-membered ring structure.

Silver(I) carboxylates tend to decarboxylate and thermally decompose at ~300 °C to give metallic silver, CO₂, and organic

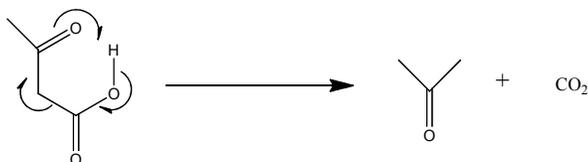
products. The temperature and mechanism of thermal reductive decomposition depends on the structure of the carboxylate moiety. For example, silver(I) benzoate decomposed at 276 °C *via* a complicated radical pathway to yield metallic silver and products such as polyphenyls derived from the radical intermediate.¹⁴ Similarly, vacuum thermal decomposition of a series of silver dicarboxylates, AgO₂C(CH₂)_{2n}CO₂Ag, n = 0–3, provided metallic silver, CO₂, and polymeric compounds derived from diradicals.¹⁵ In contrast, silver(I) acetate thermally decomposed to give metallic silver and CH₃COOH *via* formation of silver oxide and anhydride from the corresponding carboxylic acids.^{2,16,17} Silver perfluorocarboxylate, CF₃(CF₂)_nCOOAg, thermally decomposes in a similar manner.² Under decomposition conditions at temperatures greater than 200 °C, even with Ag₂O generation, Ag₂O could be thermally reduced to metallic silver.¹⁸ Therefore, uncertainty remains about whether silver ion is reduced by electron transfer during decarboxylation, or by thermal reduction of the Ag₂O formed during decomposition at temperatures above 200 °C.

The structural basis for the electron transfer process in silver acetate was studied by Olson and colleagues.¹⁹ They concluded that the Ag(I)-Ag(I) bond in silver acetate may be an important precursor to metallic silver formation, as single-electron reduction of the Ag₂(carboxylate)₂ species could result in the formation of (Ag₂)⁺ known from the chemistry of photographic processing to be a precursor of metallic silver clusters.²⁰

This body of fundamental research has promoted the development of advanced silver nanoparticles. Silver carboxylates have been used to generate silver nanoparticles, which require an organic dispersant, such as non-volatile long alkyl fatty acids.

However, the non-volatile dispersant can contaminate the metallic silver nanoparticles produced, which is undesirable.

The decarboxylation of carboxylic acids modified with certain functional groups at the α or β position smoothly proceeds *via* the formation of carbanions or radical intermediates. β -Ketocarboxylic acids, in particular, readily decarboxylate under ambient conditions *via* a six-membered transition state.



Scheme 1 Mechanism of decarboxylation of β -ketocarboxylic acids.

The goal of this study was to produce metallic silver from silver carboxylates at temperatures below 200 °C without the production of undesirable organic compounds. Despite the promise of silver(I) β -ketocarboxylates for this purpose, their preparation has not been reported, since β -ketocarboxylic acids prepared from the corresponding ester are unstable under hydrolysis conditions.²¹ Preliminary results for the preparation of several silver(I) β -ketocarboxylates have been published previously in a patent.²² The present report describes the detailed preparation of these silver(I) β -ketocarboxylates, decarboxylation in the solid state, and their structures based on infrared spectroscopy (IR) and ¹³C solid state nuclear magnetic resonance (¹³C-NMR) spectra. The calculated structures of a simple model compound and the relationship between the calculated structures and thermal decomposition also are discussed.

Experimental Section

1) Preparation

All commercially available reagents and solvents were used without further purification. Starting esters were purchased from the following chemical companies: methyl-propionylacetate (**1**) and ethyl-2-benzylacetoacetate (**8**) from Aldrich, ethyl-butylacetate (**2**) and ethyl-2-*n*-butylacetoacetate (**7**) from Alfa Aesar, methyl-*iso*-butylacetate (**3**) and ethyl-2-ethylacetoacetate (**6**) from Wako, methyl-pivaloylacetate (**4**) from Nippon Fine Chemical, and ethyl-2-methylacetoacetate (**5**) from Tokyo Kasei.

General Reaction Procedure for Silver(I) β -Ketocarboxylates (1a-8a) Sodium hydroxide (0.12 mol) was added to water (30 mL). Ethyl or methyl β -ketocarboxylate (0.1 mol) was added drop-wise to the resulting solution at approximately 60 °C. The reaction mixture was stirred for 1–4 hours at room temperature, followed by TLC (silica, *n*-hexane:ethyl acetate = 3:1). When the starting ester was detected, the reaction mixture was washed with ether to remove it. After evaporation to remove the alcohol produced by hydrolysis, the solution was cooled in an ice bath, followed by the addition of ether (50 mL) and then sulfuric acid (0.06 mol) in water (10 mL). After separation of the organic layer and extraction with ether, the combined organic layers were cooled in an ice bath. A solution of diethanolamine (0.105 mol) in water (10 mL) was added, the ether layer was removed by decantation, then an aqueous solution (10 mL) of silver(I) nitrate (0.095 mol) was added drop-wise. The resulting white precipitate was filtered, washed with chilled water and then with 2-propanol, and dried *in vacuo*.

For compound **5a**, the precipitate was soluble in water and thus was carefully washed with the minimal amount of chilled water. The silver β -ketocarboxylates obtained were stored in brown bottles at -20 °C. The compounds obtained were characterized by elemental analysis (C, H, N) (JM10; J-Science), Fourier transform infrared spectroscopy (FT-IR) (FT/IR4100; Jasco), and solid state ¹³C-NMR (Avance III 600WB; Bruker). Thermal analyses were conducted using differential scanning calorimetry (DSC) (DSC-50; Shimadzu) and thermogravimetry (TG) (DTG-50H; Shimadzu). Direct analysis in real time-mass spectrometry (DART-MS) was conducted using an AccuTOF DART (Jeol).

2) Thermolysis

Each silver(I) β -ketocarboxylate compound (50 mg) was placed in a 30-mL round bottom flask. For compounds **1a-3a**, the flask was heated in an oil bath at 150 °C; the silver salt foamed and started to decompose within 10 seconds. Immediately after foaming stopped, the products were extracted with acetone. For compound **4a**, the flask was heated at 180 °C, and for compounds **5a-8a**, the flask was heated at 130 °C. The other procedures were the same for all products. Acetone extracts were analyzed by gas chromatography-mass spectrometry (GC-MS) (GCMS-QP2010; Shimadzu) and the inorganic residues **1b-8b** were examined by X-ray diffraction (XRD) (RINT-RAPID II-S; Rigaku).

3) Computational Methods

The DFT calculations were conducted at the B3LYP²³ level of theory. A 6-31+G(d) basis set was used for C, H, and O, and an LANL2DZ²⁴ effective core potential (ECP) was used for Ag. The optimized geometries were verified by vibrational normal mode analysis. All calculations were performed using the Gaussian 03 and Gaussian 09 software packages.²⁵ The AIM calculations were performed using the AIMAll program²⁶ to evaluate the nature of the bonds in optimized structures.

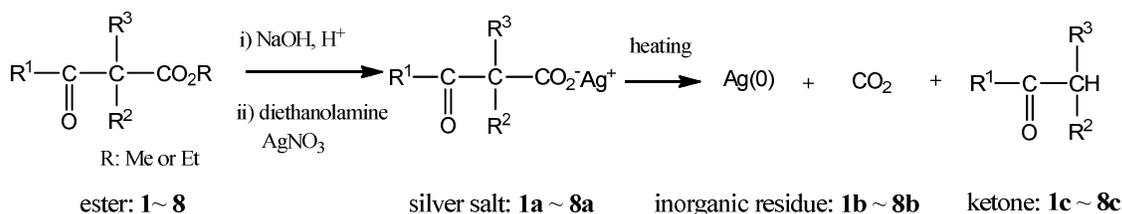
Results and Discussion

1) Preparation

Silver(I) β -ketocarboxylates were prepared as shown in **Scheme 2**. Their preparation by treating sodium β -ketocarboxylates with silver nitrate in a one-pot reaction resulted in the formation of inseparable by-products such as silver oxide. β -Ketocarboxylic acids are unstable under hydrolysis conditions²¹ and thus were carefully prepared according to a previously described procedure on hydrolysis of acetoacetic ester.²⁷ The free acid products were immediately treated with silver nitrate in the presence of diethanolamine to give the corresponding silver(I) β -ketocarboxylate. When R¹ and R² were alkyl groups (R³ = H), hydrolysis of the esters proceeded smoothly to provide high-purity silver β -ketocarboxylates, listed in **Table 1**. The crystal shapes, yields, and results of CHN analyses are described in the notes. Although the preparation of silver(I) acetoacetates also proceeded smoothly to give colorless precipitates, the resulting precipitates appeared to be unstable and turned grey. When R¹ and R² were electron-withdrawing groups [(R¹, R²) = (C₆H₅, H), (ClCH₂, H), (CH₃, C₆H₅), and (CH₃, F)] and R³ was H, silver(I) β -ketocarboxylates were formed but not isolated due to by-product formation resulting from nucleophilic attack at the β -carbonyl group. When (R¹, R², R³) = (CF₃, H, H) and (CH₃, C₂H₅, C₂H₅), silver(I) β -ketocarboxylates were not formed. The prepared

silver(I) β -keto-carboxylates adopted the keto form as determined from their IR and NMR spectra,^{notes} which are listed in **Table 1**. The resulting silver(I) β -keto-carboxylates were not soluble in

organic solvents or water; only compound **5a** showed solubility in 1-methyl-2-pyrrolidone (NMP) and in water.



Scheme 2 Preparation and thermolysis of silver(I) β -keto-carboxylates.

Table 1 Decomposition temperatures and FT-IR and solid state ^{13}C -NMR data for silver(I) β -keto-carboxylates.

Compound	R ¹	R ²	D.T. (°C)	FT-IR ^{c)} (cm ⁻¹)		Solid state ^{13}C NMR (ppm)				
				C=O	COO ⁻	C=O		COO ⁻		
1a	C ₂ H ₅ -	H-	130 - 138 ^{a)}	1715	1505	203.8	174.7			
2a	CH ₃ (CH ₂) ₂ -	H-	139 - 148 ^{a)}	1712	1505	203.7	175.1			
3a	(CH ₃) ₂ CH-	H-	139 - 150 ^{a)}	1712	1507	207.2	175.2			
4a	(CH ₃) ₃ C-	H-	167 - 176 ^{a)}	1711	1703	1532	210.6	209.1	175.2	174.1
5a	CH ₃ -	CH ₃ -	101 - 109 ^{a)}	1715	1697	1526	210.7	203.2	177.4	176
6a	CH ₃ -	C ₂ H ₅ -	102 - 121 ^{a)}	1716	1698	1540	210.2	200.9	175.7	172.8
7a	CH ₃ -	CH ₃ (CH ₂) ₃ -	110 - 119 ^{a)}	1716	1699	1542	209.6	201.3	176.0	173.6
8a	CH ₃ -	C ₆ H ₅ CH ₂ -	109 - 114 ^{a)}		1694	1555	210.6	171.6		
	Silver acetate		210 - 330 ^{b)}		1509					
	Silver laurylate		170 - 290 ^{b)}		1518					
	Silver neodecanoate		95 - 240 ^{b)}		1512					

a) measured by DSC (rate of temperature increase 10°C/min in air)

b) measured by TG (rate of temperature increase 10°C/min in air)

c) attenuated total reflection (ATR)

2) Thermolysis

2-1) DSC, TG

The thermolysis of representative silver(I) β -keto-carboxylates and silver(I) neodecanoate (used as a reference) was examined using DSC and TG; results are shown in **Figure 1** and the decomposition temperatures determined by DSC are listed in **Table 1**. Silver(I) neodecanoate melted at approximately 100 °C and gradually decomposed to give silver(0); the weight decrease occurred over a wide temperature range. Thermal analyses of silver(I) long-chain-fatty acylates reported previously¹²

decomposed over 100–250 °C. Therefore, results indicate that the decomposition of silver(I) neodecanoate is a complicated and gradual process that occurs over a wide temperature range.

In contrast, all silver(I) β -keto-carboxylates (**1a-8a**) decomposed without melting over a narrow temperature range with a rapid decrease in weight. Following decomposition (with the exception of compound **4a**), TG showed a gradual decrease until 280 °C. The gradual decrease in weight observed appeared to correspond to the ketone with a high boiling point or the dimeric ketone which is discussed in Mass spectroscopic analysis section. Exothermic peaks

were evident near 300 °C in silver(I) β -ketocarboxylates (**1a-7a**). Because generated ketones and plausible dimeric products are volatile and do not show exothermic peaks, these peaks could be attributed to aggregated Ag particles, as suggested by Logvinenko.²⁸

The TG pattern of compound **4a** showed 43.2% of the weight ratio at 176 °C remained (exothermic peak in DSC **Figure 1-i, -ii**, and notes), which corresponded to the theoretical weight ratio of Ag(0): 43.0%. No gradual decrease in weight was observed following decomposition. Little residue remained following decomposition, likely because ketone **4c** that formed had a low boiling point (106 °C) and volatilized upon Ag(0) formation during decomposition. Silver(I) β -ketocarboxylates **4a** clearly demonstrated simultaneous decomposition and reduction of Ag⁺.

The TG of compound **8a** differed from the other silver(I) β -ketocarboxylates: only a 14.6% weight loss was measured during decomposition at 97–104 °C, and weight loss continued gradually

following decomposition. The observed weight loss at 97–104 °C corresponded to the weight ratio of CO₂ in compound **8a**: 14.7%, indicating that metallic silver and the corresponding ketone **8c** (b.p. 235 °C) or the dimeric product remained at the decomposition temperature.

In compound **5a**, 42.8% of the weight was lost at 109 °C (the decomposition temperature), corresponding to 83.0% of the weight of the organic moiety. Subsequently, the weight gradually decreased to 50.6% of the original mass of compound **5a** (98.1% of the weight of the organic moiety) at 350 °C. As the theoretical weight ratio of Ag(0) is 48.4%, the plausible dimeric or trimeric ketone must have remained.

TG analysis of compounds **1a-3a**, **6a**, and **7a** showed patterns similar to that of compound **5a**. The theoretical weight ratio of Ag, and the residual weight ratios at 280 °C, 350 °C, and just after decomposition are described in the notes.

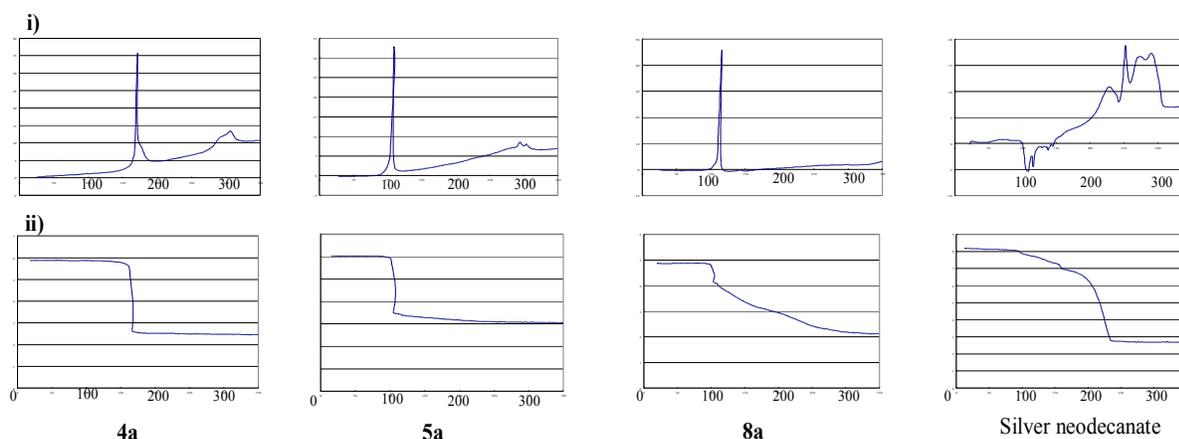


Figure 1 i) DSC of silver(I) β -ketocarboxylates (**4a**, **5a**, **8a**) and silver(I) neodecanoate. ii) TG of silver(I) β -ketocarboxylates (**4a**, **5a**, **8a**) and silver(I) neodecanoate. Rate of temperature increase: 10 °C/min in air

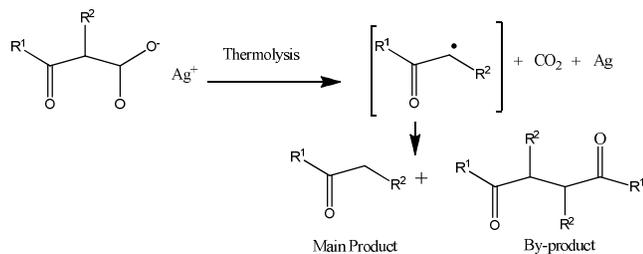
2-2) Mass spectroscopic analysis of products formed during thermolysis

The products formed during thermolysis were analyzed by mass spectroscopy; detailed results are presented in the notes.

The products formed by thermolysis from compounds **1a-8a** at their decomposition temperatures (see Experimental Section) were extracted with acetone and examined by GC-MS. Thermolysis of compound **8a** at 130 °C provided a peak corresponding to **8c**: 4-phenyl-2-butanone with a boiling point of 235 °C. The gradual decrease between 200 and 250 °C in the TG curve of compound **8a** in **Figure 1-ii** was attributed to thermal behavior of **8c**. Similarly, thermolysis of compound **7a** at 130 °C provided a peak corresponding to **7c**, 2-heptanone (MW 114), with a boiling point of

150 °C, and a weak peak corresponding to the dimer (MW 226). For compounds **1a-6a**, the corresponding ketones **1c-6c** were not detected as their boiling point is lower than the temperature used for thermolysis.

Powdery silver(I) β -ketocarboxylates were analyzed by DART-MS using a 300 °C ion source. Compounds **1a-8a** gave peaks corresponding to the molecular weights ($M_{1c-8c} + 1$) of their corresponding ketones, **1c-8c**. In addition, intense peaks with a molecular weight of ($2M_{1c-8c} - 1$), due to dimerized radical intermediates, and peaks corresponding to the trimer ($3M_{1c-8c} - 3$) were observed. Although GC-MS data of peaks corresponding to dimers do not prove their formation during thermolysis, the results suggest the formation of keto-radicals during thermolysis.



Scheme 3 Mechanism of thermolysis of silver(I) β -ketocarboxylates.

Formation of the ketone and dimer may explain the gradual decrease in weight following decomposition and the exothermic peaks around 300 °C in the TG data. Volatilization of the resulting ketones and dimer provided endothermic peaks. Thus, in each case, the gradual decrease in weight following decarboxylation corresponded to volatilization of the dimer and resulting ketone with boiling points at temperatures greater than 200 °C, whereas the exothermic peak near 300 °C can be attributed to aggregation of the Ag particles.

2-3) Chemical composition analysis of the inorganic residue

Silver(I) β -ketocarboxylates **1a-8a** thermally decomposed at temperatures below 190 °C. At these temperatures, if the mechanism of decomposition occurred *via* acid anhydride and Ag_2O , similar to those in silver carboxylates,^{2,16,17} Ag_2O should be formed. The Ag_2O was not thermally reduced to afford metallic silver at temperatures below 190 °C.¹⁸ The inorganic residues were examined using XRD after conducting thermolysis at the decomposition temperatures. No silver oxides or silver salt (Ag_2O , AgO , or AgCO_3) were observed after thermolysis: only $\text{Ag}(0)$ was found.

Decomposition by decarboxylation was complete at temperatures below 190 °C. The resulting products included metallic silver and organic compounds derived from the corresponding ketoradical. These results clearly suggest that silver oxide was not involved in these reactions and that metallic silver, ketoradicals, and CO_2 were formed.

3) Structure

3-1) FT-IR and solid state ^{13}C -NMR data for silver(I) β -ketocarboxylates

Characteristic spectroscopic data and decomposition temperatures of the isolated silver(I) β -ketocarboxylates **1a-8a** are listed in **Table 1**. Representative solid state ^{13}C -NMR spectra are shown in **Figure 2**. The IR spectra of compounds **1a**, **2a**, and **3a** showed a band corresponding to β -carbonyl groups at 1712–1715 cm^{-1} and strong bands corresponding to carboxylate groups at 1505–1507 cm^{-1} . Solid state ^{13}C -NMR spectra of these compounds showed single signals for the β -carbonyl and carboxylate groups.

In contrast, the IR spectra of compounds **4a-7a** contained two bands corresponding to β -carbonyl groups, at 1711–1716 cm^{-1} and at 1697–1703 cm^{-1} , and bands for their carboxylate groups at 1526–1542 cm^{-1} . The solid state ^{13}C -NMR spectra of compounds **4a-7a** showed two signal groups for the β -carbonyl and carboxylate groups.

The IR spectrum of compound **8a** showed a band corresponding to the β -carbonyl group at 1694 cm^{-1} and of the carboxylate group at 1555 cm^{-1} . In contrast with the solid state ^{13}C -NMR spectra of compounds **1a-3a**, there is a signal at lower magnetic field (210.6 ppm) for the β -carbonyl group and a signal for the carboxylate group at higher magnetic field (171.6 ppm). This signal pattern was simpler than those of compounds **5a-7a**. The signals near 210.6 ppm seen in **Figures 2-8a** were attributed to side bands.

Absorption bands and ^{13}C -NMR signals arising from the carbonyl group at the β -position and from the carboxylate group suggested the presence of a number of coordination modes involving the carbonyl group.

3-2) Proposed Structures

The carbonyl group in silver(I) β -ketocarboxylates may coordinate the silver ion. This suggests structures other than the eight-membered ring coordination of silver salts of fatty acids, as shown in **Figure 3**. **Type I** is the same type as silver salts of fatty acids. In **Type II**, one of the two carbonyl groups is involved in the coordination. **Type III** coordinates the silver ion between two COO -groups and two C=O groups. Spectroscopic features of these different types of coordination can be predicted empirically as follows. For the **Type III** structure, the IR absorption bands of the β -carbonyl group would shift to lower wavenumbers and those of the carboxylate groups would shift to higher wavenumbers compared with the corresponding absorption bands of **Type I** compounds. In **Type II** coordination, two IR absorption bands are seen. Solid state ^{13}C -NMR of **Type III** compounds show the β -carbonyl group signal shifted to lower magnetic field and the carboxylate group signal shifted to higher magnetic field compared with the corresponding signals in **Type I** compounds. In **Type II** compounds, two signals for each C=O group and each COO - group can be seen.

3-3) Classification of silver(I) β -ketocarboxylates

Compounds **1a-8a** were classified into **Types I-III** based on their spectra. Compounds **1a**, **2a**, and **3a** showed spectra similar to silver(I) aliphatic carboxylates and were therefore classified into the **Type I** structure. The spectroscopic patterns obtained for compound **8a** corresponded with the expected pattern for **Type III** compounds: the absorption bands of the β -carbonyl group shifted to lower wavenumbers and those of the carboxylate groups shifted to higher wavenumbers than the corresponding absorption bands of compounds **1a**, **2a**, and **3a**. The solid state ^{13}C -NMR signal of the β -carbonyl group shifted to lower magnetic field and the signal from the carboxylate group shifted to higher magnetic field compared with **Type I** compounds. When compound **8a** adopted a **Type III** structure with the twelve-membered ring, steric repulsion by the benzyl groups may decrease compared to a **Type I** structure.

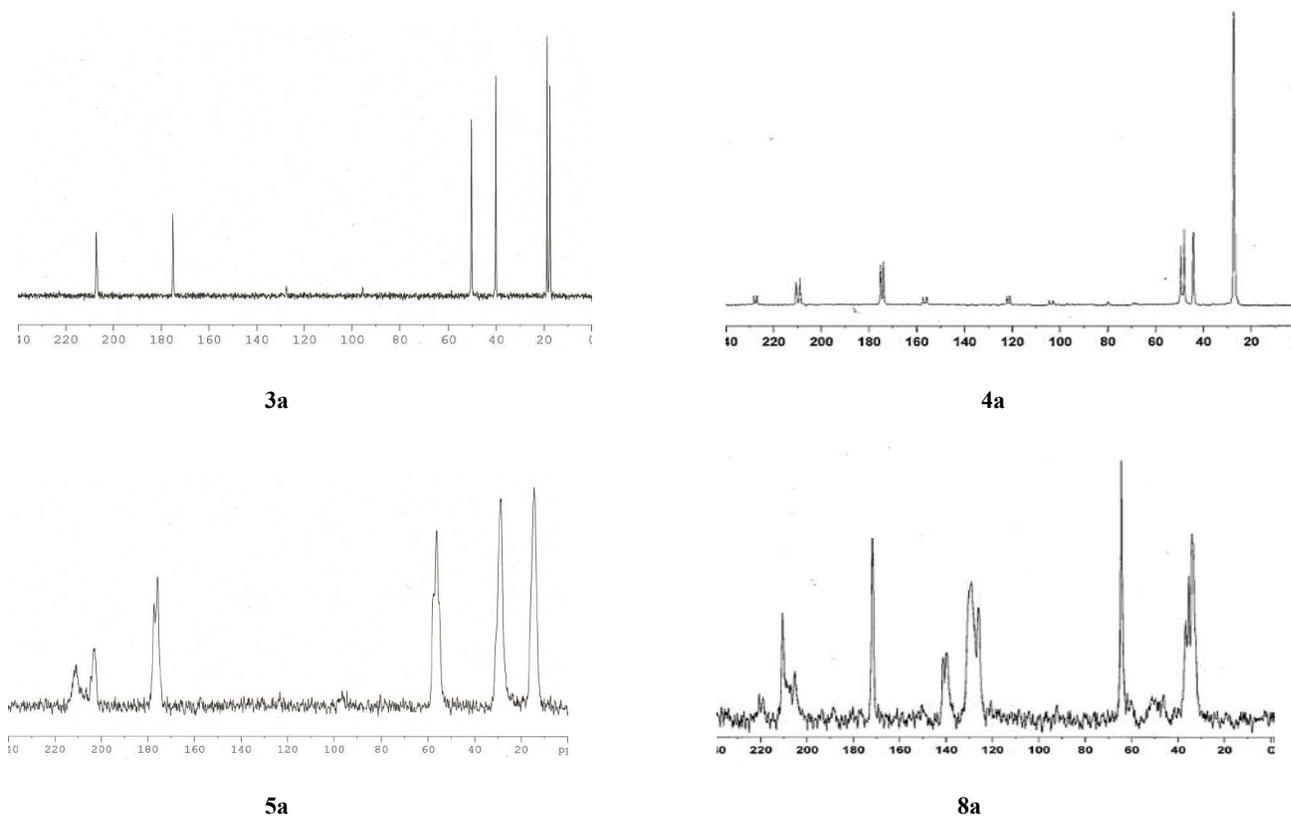


Figure 2 Typical solid state ^{13}C -NMR spectra.

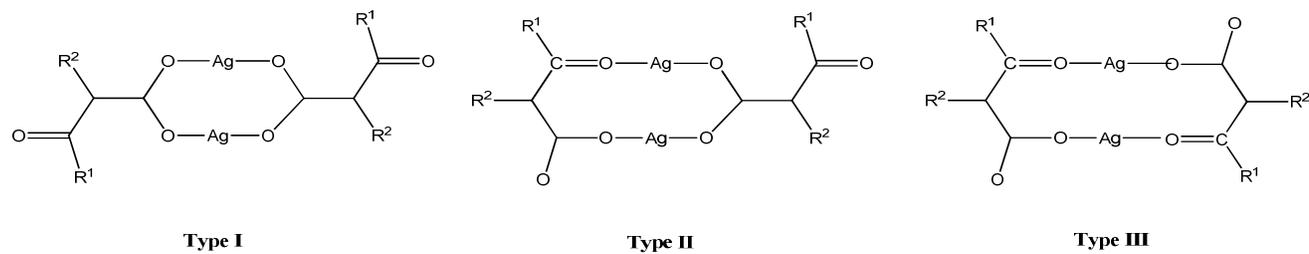


Figure 3 Plausible structures of silver(I) β -ketocarboxylates.

Journal Name

Steric repulsion by the substituents at the α positions of compounds **5a**, **6a**, and **7a** should be less than that in compound **8a**. The spectra suggest that compounds **5a**, **6a**, and **7a** may adopt a **Type II** or mixture of **Type I** and **III** structures. A sharp exothermic peak was present at low temperatures. If these compounds were a mixture of **Type I** and **III** structures, the exothermic peak would be broad. But from this point, they are more likely to adopt **Type II**.

The spectrum of compound **4a** showed patterns similar to those of compounds **5a-7a**, with some differences. In the solid state ^{13}C -NMR of compounds **5a-7a**, two broad signals for C=O and COO-groups were present. In the IR spectra of compounds **5a-7a**, the differences between the wavenumbers of the two absorption bands for carbonyl groups C=O were in the range of 17–18 cm^{-1} . In contrast, in the solid state ^{13}C -NMR of compound **4a**, two sharp signals and a small chemical shift difference between the carbonyl signals were observed. In the IR spectrum of compound **4a**, two absorption bands for a carbonyl group C=O were observed at wavenumbers above 1700 cm^{-1} , with a difference between the wavenumbers of 8 cm^{-1} , which differed from the shifts: 17–18 cm^{-1} as seen in **Type II**: compounds **5a-7a**. These spectroscopic differences might be attributed to stereoisomers of compound **4a** with a **Type I** rather than **Type II** structure in the crystals.

Based on the spectroscopic data, compounds **1a-4a**, compounds **5a-7a**, and compound **8a** were categorized as **Type I**, **Type II**, and **Type III**, respectively. Definitive assignment required determining the structures of the proposed types by X-ray analysis and EXAFS, but this was not possible due to practical difficulties.

3-4) DFT calculations and AIM analysis of silver(I) β -ketocarboxylates

Possible structures of silver(I) β -ketocarboxylates were investigated using structural calculations of a model compound lacking substituents. The compound, $\text{HCOCH}_2\text{COOAg}$ [$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$], was chosen to investigate a wide range of skeletal structures due to flexibility (no rotational hindrance caused by substituents).

The structures optimized for symmetry and potential energy and the results of AIM calculations are illustrated in **Figure 4**. The bond critical points (BCP) are shown as green dots and the ring critical points (RCP) are shown as red dots. The bond paths with an electron density value (ρ) at a BCP below 0.025 a.u. are drawn as dashed lines instead of solid lines. Optimized energies of the five resulting categories of structures, their relative energies, and the calculated IR vibrational frequencies of the intense COO- and C=O stretching modes are listed in **Table 2**. Selected bond lengths and AIM properties at each BCP are listed in **Table 3** (supporting information).

The resulting structures were divided into three main categories. **Type I** is an eight-membered ring structure, which is the same structure as the well-known silver carboxylate dimers.⁸ Several conformers of this type differing in rotational bond angle between the α -carbon and carboxylate carbon were found in this study. **Figures 4(a)** and **(b)** show examples of C_i symmetry and C_{2h} symmetry structures, respectively. Only small differences in the energy and ring structural parameters exist in **Type I** conformers; in addition, the Ag(1)-Ag(2) distances were all approximately 2.83 Å, and BCPs were found between Ag(1) and Ag(2). Two RCPs were found at each AgOCOAg five-membered ring. These

results are in good agreement with the experimental and theoretical results of related complexes reported previously.¹⁹

Type 2 structures have one side that forms the same five-membered ring as in **Type 1** compounds, whereas the other side forms three-oxygen coordination. Carboxylate oxygen O(4) coordinated to Ag(1), and carboxylate oxygen O(5) and carbonyl oxygen O(6) coordinated to Ag(2), as shown in **Figure 4(c)**. Two rotational conformers existed around the α -carbon and carboxylate carbon bond that differed only slightly in energy (< 0.1 kcal/mol). The Ag-Ag bond length was calculated to be 2.988 Å, indicating metallophilic interaction²⁹.

In **Type 3**, both carboxylates coordinate with two silver atoms through three-oxygen coordination. Two distinct structures were evident with significantly different Ag(1)-Ag(2) distances (3.297 Å and 3.669 Å). **Type 3a** has C_2 symmetry, whereas **Type 3b** has C_i symmetry. AIM results indicated that **Type 3a** had a weak BCP, whereas **Type 3b** had no BCP between Ag(1) and Ag(2).

Of the types of structures obtained, **Type 1** is the most stable, followed by structure **Type 2**, whose calculated energy is about 5 kcal/mol greater than that of **Type 1a**. The calculated energy of **Type 3b** is about 9 kcal/mol greater than that of **Type 1a**; that of **Type 3a**, the least stable structure is about 10 kcal/mol greater than that of **Type 1a**. These relative energies indicate that all four structure types can exist stably or isomerize easily due to the small energy differences between them.

The calculated vibrational frequencies of the COO- and C=O groups are listed in **Table 2**. **Type 2** compounds showed two peaks arising from C=O stretching of the β -carbonyl groups. In contrast, for **Type 3**, the peak of the β -carbonyl group shifted to lower wavenumber compared to the corresponding β -carbonyl group of **Type 1**. From these results, it is possible that the **Type 1** structure calculated here corresponds to **Type I** of the plausible structure shown in **Figure 3**, **Type 2** corresponds to **Type II**, and **Type 3** corresponds to **Type III**.

These computational results allowed the re-examination of the structures of the compounds synthesized in this study. The above discussion regarding two isomers, such as **Type 1a** and **Type 1b**, in the eight-membered ring structure is pertinent to compound **4a**. DFT calculations clearly showed the presence of isomers with very similar energy levels; furthermore, the difference observed between the wavenumbers of the C=O groups, 8 cm^{-1} , was consistent with the calculated difference. Thus, the observed spectroscopic differences can be attributed to stereoisomers of compound **4a** with a **Type I** structure. As predicated by the calculated isomers, each carbon showed two signals, as seen in **Figures 2-4a**.

The structure of compound **8a** was assigned to **Type III** based on the spectroscopic patterns. DFT calculations showed two possible coordination types: **Types 3a** and **3b**, depicted in **Figure 4**. The Ag-O=C bond length in **Types 2** and **3a** was 2.603 Å and 2.641 Å, respectively; however, a shorter bond length of 2.410 Å was calculated for **Type 3b**. Thus, the bond strength of Ag-O=C in **Type 3b** is stronger than in **Types 2** and **3a**. In accordance with the strong Ag-O=C bond strength, the FT-IR spectrum of compound **8a** shows C=O shifted to lower wavenumber. In addition, the observed COO absorption bands are similar to the calculated bands. Therefore, the structure of compound **8a** is more likely **Type 3b** rather than **Type 3a**.

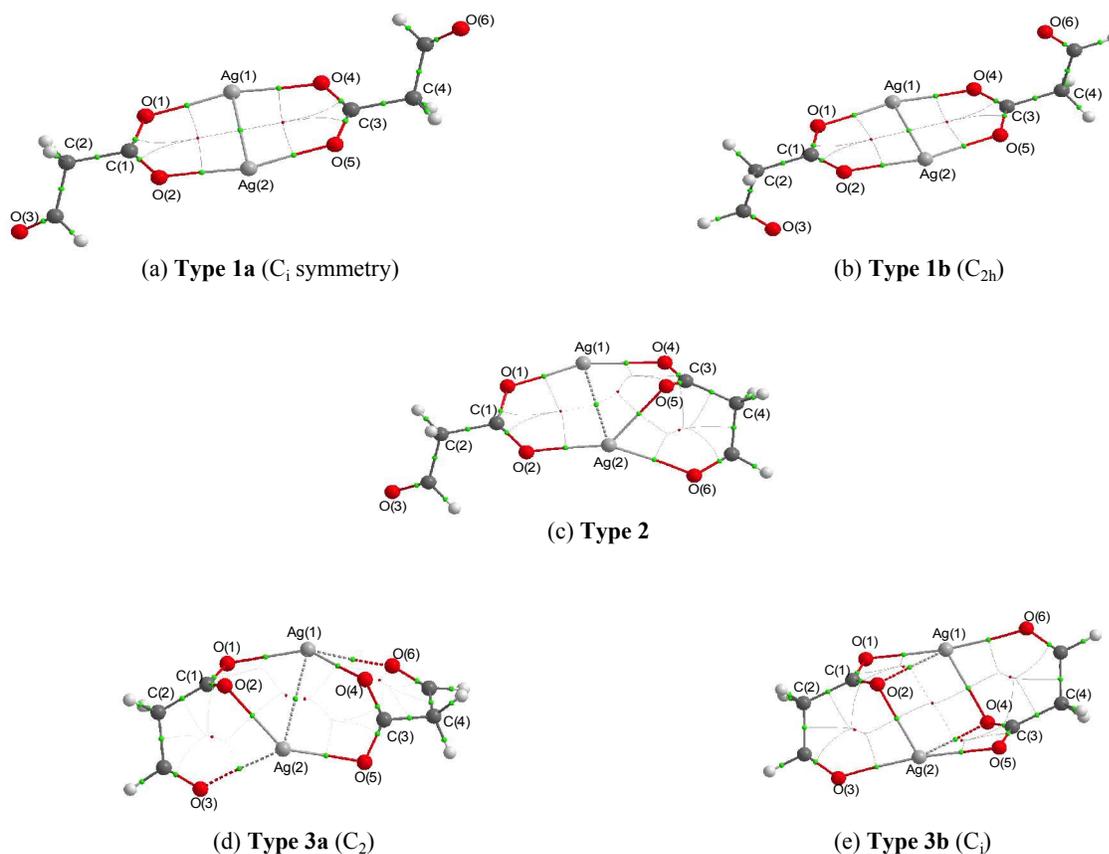


Figure 4 Optimized structures of silver β -ketocarboxylates. The green dots show BCPs and small red dots show RCPs. The electron density threshold value for defining “weak” BCPs is 0.025 a.u.

Table 2 Calculated energies and vibrational frequencies of COO⁻ and CO stretching modes with strong IR intensities.

	E (hartree)	ΔE^a (kcal/mol)	$\Delta E_{ZPE}^{a,b}$ (kcal/mol)	$\nu(\text{COO}^-)$ (cm^{-1})	$\nu(\text{CO})$ (cm^{-1})
Type 1a	-975.256926	(0)	(0)	1621	1810
Type 1b	-975.254536	1.5	1.5	1631	1819
Type 2	-975.248007	5.6	5.4	1628	1778, 1808
Type 3a	-975.239913	10.7	10.3	1625	1787
Type 3b	-975.242649	9.0	8.6	1645	1778

a) Relative energies to Type 1a.

b) Including vibrational zero point energy correction.

4) Relationship between thermal decomposition and structure

The factors affecting the formation of metallic silver upon thermal decomposition of silver(I) carboxylates have been discussed in terms of bonding strength to the Ag^+ , the structure of the intermediate,¹⁹ and the length of the Ag-Ag bond.¹⁰ Similarly, the thermal decomposition of silver(I) β -ketocarboxylates **1a-8a** were examined. As discussed above, the thermal decomposition temperature of compounds **1a-4a** (130–176 °C), compounds **5a-7a** (101–121 °C), and compound **8a** (109–114 °C), coupled with spectroscopic data and the results of AIM calculations, suggest these compounds be categorized as **Type 1a** or **1b**, **Type 2**, and **Type 3a** or **Type 3b**, respectively.

Burleva examined the relationship between decomposition temperature and structure of silver dicarboxylates $\text{AgO}_2\text{C}(\text{CH}_2)_n\text{CO}_2\text{Ag}$ and determined that decomposition temperature depended on the strength of the Ag-O bond.¹⁵ The bond strength between Ag and the oxygen atom of the carboxylate group in **Type 3a** [ρ value: 0.0477 for Ag(1)-O(4)], **Type 3b** [ρ value: 0.0217 for Ag(1)-O(2)], and **Type 2** [ρ value: 0.0467 for Ag(2)-O(5)] are weaker than those of **Types 1a** and **1b** (ρ value: ca. 0.068). The decrease in ρ value of **Type 3a**, **Type 3b**, and **Type 2** compounds was attributed to the coordination of Ag^+ by the C=O group. According to the relationship suggested by Burleva, a decrease in the bond strength between the Ag ions and carboxylates decreases the decomposition temperature. Compounds categorized as **Types 2**, **3a**, and **3b**, which have lower ρ values, are expected to decompose at lower temperatures than **Type 1a** and **1b** compounds. In fact, compounds **1a-4a**, categorized as **Type 1a** or **1b**, decomposed at 130–176 °C, and compounds **5a-8a**, categorized as **Types 2**, **3a**, and **3b**, decomposed at 101–121 °C. Thus, the thermal decomposition temperature of silver(I) β -ketocarboxylates depended on the strength of the bond between Ag and the oxygen atom of the carboxylate group; a decrease in strength due to C=O group participation caused a decrease in the decomposition temperature.

Compounds **1a-4a** were categorized as **Types 1a** and **1b**; no coordination occurred between the Ag^+ and the C=O groups, but C=O group participation might occur during the thermal decomposition. As shown in **Table 1**, the decomposition temperature increased with the bulkiness of R^1 . The small differences in potential energy (< 10 kcal/mol) indicate that each type could be converted to another type. Thus, the calculations conducted on the model compound suggested that the C=O group may participate in coordination to Ag^+ during thermal decomposition. It is likely that increased bulkiness may disrupt coordination by the C=O group. In the **Type I** compounds **1a-4a**, an increase in the bulkiness of R^1 increased the decomposition temperature. Furthermore, simple silver aliphatic carboxylates lacking a C=O group decomposed at temperatures above 200 °C, indicating that the coordination of C=O to Ag ion lowers the decomposition temperature.

Silver(I) β -ketocarboxylates **1a-8a** were characterized by both their lower decomposition temperature and abrupt decomposition observed by thermal analysis. The abrupt decomposition indicates the decomposition mechanism. Products derived from keto-radicals were observed by mass analysis. Observation of keto-radical-derived products coupled with the results of DFT and AIM calculations allowed the proposal of a mechanism of decomposition. The coordination of C=O to Ag ion may lead to formation of $(\text{Ag}_2)^{++}$ by electron transfer, as well as by the single electron-reduction proposed by Olson.¹⁹ In particular, the structure of **Type 2** and **Type 3a** compounds are similar to that of the intermediate, making them conducive to electron transfer. After

electron transfer, successive bond-cleavages yield products derived from the keto radical, CO_2 , and metallic silver.

The short Ag-Ag bond suggested by Tolochko¹⁰ is likely to be advantageous for the formation of $(\text{Ag}_2)^{++}$ by electron transfer. The Ag-Ag distance in the dimeric structure in **Types 1a** and **1b**, **Type 2**, and **Type 3a** obtained by AIM calculations were 2.831–3.29 Å, similar to that of simple silver aliphatic carboxylates. However, **Type 3b** compounds showed a non-bonding Ag-Ag bond distance (3.669 Å). Compound **8a** belongs to **Type 3b** and yet decomposed abruptly at 109–114 °C. Consequently, the effect of the bond distance between Ag-Ag needs to be reconciled with the calculations for structural changes of compound **8a** and/or the model compound with the observed formation of silver radical cation.

Initially, silver(I) β -ketocarboxylates were expected to decompose inherently *via* the well-known six-membered ring transition state, similar to that shown in **Scheme 1**, or silver(I) carboxylates were expected to decompose *via* Olson's intermediate. The calculated structures suggested that the decomposition of dimeric **Type 2** and **Type 3a, b** compounds may proceed *via* a deformed six-membered ring transition state involving the C=O group, and that in **Type 1a** and **b** compounds, the structures may be deformed to a **Type 2** or **Type 3**-like structure. Thus, the substituent of R^2 decides the Types of the structures and in **Type 1**: compound **1a-4a**, increasing the bulkiness of R^1 , transformation to the expected intermediate: **Type 2**- or **Type 3a**-like intermediate requires higher temperature. The characteristic sharp thermal decompositions of silver(I) β -ketocarboxylate at lower temperatures can be attributed to the coordination of the C=O group to the Ag^+ ion. Viewed from another perspective, the decomposition temperature can be controlled by intramolecular or intermolecular coordination to the Ag^+ ion.³⁰ To understand the decomposition processes in detail, the structures of silver(I) β -ketocarboxylates with R^1 and R^2 substituents are currently being determined.

Conclusions

A series of silver(I) β -ketocarboxylates were prepared by reaction of β -ketocarboxylic acids from the corresponding esters with silver nitrate in the presence of diethanolamine. The obtained silver(I) β -ketocarboxylates thermally decomposed at lower temperature than silver(I) aliphatic carboxylates over a narrow temperature range and afforded metallic silver, volatile ketones, and CO_2 . Product analysis by DART-MS and GC-MS indicated the involvement of radical intermediates during decomposition.

Differences in the decomposition temperatures of silver(I) β -ketocarboxylates, together with IR and solid ¹³C-NMR spectral data, allowed their classification into three structural categories: **Type I**, as well as silver(I) stearate with an eight-membered ring structure, **Type II**, and **Type III**. The β -carbonyl group is proposed to be involved in coordinating Ag^+ in **Type II** and **Type III** compounds. The proposed structures were verified by calculating the structures of a simple model compound, $\text{HCOCH}_2\text{COOAg}$, using DFT and AIM methods. Three types of calculated structures, **Types 1a-b**, **Type 2**, and **Type 3b**, corresponded to the proposed structures **Type I**, **Type II**, and **Type III**, respectively. The three categories differed significantly in Ag-O bond strength. The decreased bond strength of the Ag-O bond caused by C=O group participation lowered the decomposition temperature. Coordination of C=O to Ag ion resulted in smooth electron transfer during decomposition to yield $(\text{Ag}_2)^{++}$. The apparent similarity of the **Type 2** and **Type 3a** structures to the intermediate made compounds **5a-8a** favorable

ARTICLE

for electron transfer. After electron transfer, successive bond-cleavages yielded products derived from the keto radical, as well as CO₂ and metallic silver.

Silver(I) β-ketocarboxylates thermally decompose into volatile ketones and metallic silver without the need for a chemical reducing reagent. Consequently, silver(I) β-ketocarboxylates are potent compounds for the formation of metallic silver by thermal decomposition and are a useful source of metallic silver for industrial materials.

Acknowledgements

We wish to express our gratitude to Ms. Asano, Dr. Shu, Mr. Haneoka, and Mr. Matsuzaki of the Comprehensive Analysis Center at ISIR, Osaka University. This work was partially supported by NEDO JAPER project in 2014.

Notes

Silver(I) n-propionylacetate (Silver(I) 3-oxopentanoate) (1a): colorless microcrystals; 80% yield; ¹³C NMR (600MHz, Solid); δ 6.8(CH₃), 34.9(CH₃CH₂CO), 51.2(COCH₂CO₂), 174.7(CO₂-), 203.8(CO); Elemental analysis (measured values; C 26.87, H 2.95, calculated values; C 26.93, H 3.16); TG(138°C 55.7%, 280°C 51.5%, 350°C 50.5%, theoretical silver content 48.4%); DART-MS (ESI+, 12V) m/z 73 (M' + 1) 9, 143 (2M' - 1)100, 213 (3M' - 3)44, (M' = M - (CO₂Ag) + 1: C₂H₅COCH₃);

Silver(I) n-butyrylacetate (Silver(I) 3-oxohexanoate) (2a): colorless microcrystals; 76% yield; ¹³C NMR (600MHz, Solid); δ 12.9(CH₃), 16.5(CH₃CH₂), 44.2(CH₂CH₂CO), 52.2(COCH₂CO₂), 175.1(CO₂-), 203.7(CO); Elemental analysis (measured values; C 30.39, H 3.69, calculated values; C 30.40, H 3.84); TG(148°C 55.7%, 280°C 48.9%, 350°C 47.8%, theoretical silver content 45.6%); DART-MS (ESI+, 12V) m/z 87 (M' + 1) 6, 171 (2M' - 1)100, 255 (3M' - 3)31, (M' = M - (CO₂Ag) + 1: CH₃(CH₂)₂COCH₃);

Silver(I) iso-butyrylacetate (Silver(I) 4-methyl 3-oxopentanoate) (3a): colorless microcrystals; 83% yield; ¹³C NMR (600MHz, Solid); δ 17.5(CH₃CH), 18.7(CH₃CH), 40.2(CHCO), 50.4(COCH₂CO₂), 175.2(CO₂-), 207.2(CO); Elemental analysis: (measured values C 30.33 H 3.65 calculated values C 30.41 H 3.84); TG(150°C 51.9%, 280°C 46.3%, 350°C 45.5% theoretical silver content 45.6%); DART-MS (ESI+, 12V) m/z 87 (M' + 1)15, 171 (2M' - 1)100, 255 (3M' - 3)51, (M' = M - (CO₂Ag) + 1: (CH₃)₂CH₂COCH₃);

Silver(I) t-pivaloylacetate (Silver(I) 4,4-dimethyl 3-oxopentanoate) (4a): colorless microcrystals; 84% yield; ¹³C NMR (600MHz, Solid); δ 27.0, 27.2(CH₃), 44.0, 44.3(CCO), 48.0, 49.4(COCH₂CO₂), 174.1, 175.2(CO₂-), 209.1, 210.6(CO); Elemental analysis: (measured values C 33.42 H 4.47 calculated values C 33.49 H 4.42); TG(176°C 43.2%, 280°C 42.3%, 350°C 41.8% theoretical silver content 43.0%); DART-MS (ESI+, 12V) m/z 101 (M' + 1)31, 199 (2M' - 1)67, 279 (2M' + 79, 3M' - 3 - 18)100, 297(3M' - 3)49, (M' = M - (CO₂Ag) + 1: (CH₃)₃CCOCH₃);

Silver(I) β-methylacetoacetate (Silver(I) 2-methyl 3-oxobutyrate) (5a): colorless microcrystals; 65% yield; ¹³C NMR

(600MHz, Solid); δ 14.6(CH₃CH), 28.7, 29.0(CH₃CO), 56.4, 57.7(COCHCO₂), 176.0, 177.4(CO₂-), 202.9, 203.2, 210.7, 211.1(CO); Elemental analysis (measured values; C 26.64, H 2.88, calculated values; C 26.93, H 3.16); TG(109°C 57.2%, 280°C 51.1%, 350°C 50.6% theoretical silver content 48.4%); DART-MS (ESI+, 12V) m/z 73 (M' + 1)61, 143 (2M' - 1)100, 195(2M + 51)42, (M' = M - (CO₂Ag) + 1: CH₃COC(CH₃)₂H₅);

Silver(I) β-ethylacetoacetate (Silver(I) 2-ethyl 3-oxobutyrate) (6a): colorless microcrystals; 71% yield; ¹³C NMR (600MHz, Solid); δ 13.0(CH₃CH₂), 22.2, 25.0(CH₃CH₂CH), 29.0, 30.9(CH₃CO), 60.6, 63.0, 63.9, 68.3(COCHCO₂), 172.8, 173.5, 175.7(CO₂-), 200.9, 204.2, 210.2(CO); Elemental analysis(measured values; C 30.11, H 3.68, calculated values; C 30.40, H 3.84); TG(121°C 53.2%, 280°C 47.3%, 350°C 46.4% theoretical silver content 45.6%) DART-MS (ESI+, 12V) m/z 87 (M' + 1)38, 171 (2M' - 1)100, 255 (3M' - 3)7, (M' = M - (CO₂Ag) + 1: CH₃CO(CH₂)₂CH₃);

Silver(I) β-n-butyrlacetoacetate (Silver(I) 2-n-butyl-3-oxobutyrate) (7a): colorless microcrystals; 84% yield; ¹³C NMR (600MHz, Solid); δ 13.8(CH₃CH₂), 22.2, 23.5, 25.5, 26.5(CH₂), 29.9, 31.5(CH₃CO), 60.4, 62.2, 62.5, 65.0(COCHCO₂), 172.5, 173.6, 176.0, 177.6(CO₂-), 201.3, 202.9, 209.6, 210.6, 211.0(CO); Elemental analysis (measured values; C 36.14, H 4.86, calculated values; C 36.25, H 4.94); TG(119°C 53.2%, 280°C 41.7%, 350°C 40.0% theoretical silver content 40.8%)DART-MS (ESI+, 12V) m/z 115 (M' + 1)59, 227 (2M' - 1)100, 339 (3M' - 3)9, (M' = M - (CO₂Ag) + 1: CH₃CO(CH₂)₄CH₃);

7c: GC-MS M' - 71(43) = 100, M' - 56(58) = 58.14, M' - 43(71) = 15.12, M' - 29(85) = 2.32, M' - 15(99) = 1.74, M'(114) = 2.91

Silver(I) β-benzylacetoacetate (Silver(I) 2-n-benzyl-3-oxobutyrate) (8a): colorless microcrystals; 83% yield; ¹³C NMR (600MHz, Solid); δ 33.8(CH₃), 35.3, 36.6(CH₂), 64.3(COCHCO₂), 126.0, 129.0, 139.9, 141.3(C₆H₅), 171.6(CO₂-), 210.6(CO); Elemental analysis (measured values; C 44.02, H 3.52, calculated values; C 44.18, H 3.71); TG(97°C 99.4%, 104°C 84.8% 114°C 81.0% 280°C 46.5%, 350°C 43.6% theoretical silver content 36.1%); DART-MS (ESI+, 12V) m/z 149 (M' + 1)36, 295 (2M' - 1)100, 441 (3M' - 3)12, (M' = M - (CO₂Ag) + 1: CH₃CO(CH₂)₂C₆H₅);

8c: GC-MS M' - 105(43) = 100, M' - 97(51) = 15.85, M' - 83(65) = 12.20, M' - 71(77) = 21.95, M' - 57(91) = 63.41, M' - 43(105) = 92.68, M' - 33(115) = 4.88, M' - 15(133) = 14.63, M'(148) = 52.44

References

- 1 P. Uznanski and E. Bryszewska, *J Mater Sci.*, 2010, **45**, 1547.
- 2 R. Szczesny and E. Szlyk, *J Therm. Analn Calorim.*, 2013, **111**, 1325.
- 3 Y. U. Seo, S. J. Lee and K. Kim, *J. Phys. Chem. B*, 2004, **108**, 4000.
- 4 K. Kim, H. S. Lee and H. M. Kim, *Vibrational Spectroscopy*, 2007, **44**, 308.

Journal Name

- 5 (a) S. F. Jahn, A. Jakob, T. Blaudeck, P. Schmidt, H. Lang and R. R. Baumann, *Thin Solid Films*, 2010, **518**, 3218; (b) S. F. Jahn, T. Blaudeck, R. R. Baumann, A. Jakob, P. Ecorchard, T. Ruffer and H. Lang, *Chem. Mater.*, 2010, **22**, 3067.
- 6 V. Vand, A. Aitken and R. K. Campbell, *Acta Cryst.*, 1949, **2**, 398.
- 7 A. E. Blakeslee and J. L. Hoard, *J. Am. Chem. Soc.*, 1956, **78**, 3029.
- 8 C. B. Acland and H. C. Freeman, *Chemical Communications*, 1971, 1016.
- 9 X. M. Chen and T. C. W. Mak, *J. Chem. Soc. DALTON TRANS*, 1991, 1219.
- 10 B. P. Tolochko, S. V. Chernov, S. G. Nikitenko and D. R. Whitcomb, *Nuclear Instruments and Methods in Physics Research A*, 1998, **405**, 428.
- 11 S. J. Lee, S. W. Han, H. J. Choi and K. Kim, *J. Phys. Chem. B*, 2002, **106**, 2892.
- 12 B. B. Bokhonov, A. A. Sidelnikov, M. R. Sharafutdinov, B. P. Tolochko, L. P. Burleva and D. R. Whitcomb, *J. Imaging Sci. Technol.*, 2003, **47**, 89.
- 13 K. Binnemans, R. V. Deun, B. Thijs, I. Vanwelkenhuysen and I. Geuens, *Chem. Mater.*, 2004, **16**, 2021.
- 14 E. K. Fields and S. Meyerson, *J. Org. Chem.*, 1976, **41**, 916.
- 15 L. P. Burleva, V. M. Andreev and V. V. Boldyrev, *Journal of Thermal Analysis*, 1988, **33**, 735.
- 16 A. D. Kirshenbaum, A. G. Streng and M. Hauptschein, *J. Am. Chem. Soc.*, 1953, **75**, 3141.
- 17 M. D. Judd, B. A. Plunkett and M. I. Pope, *Journal of Thermal Analysis*, 1974, **6**, 555.
- 18 H. C. Vacher, *Metals Handbook*, The American Society for Metals, Cleveland, Ohio, 1948, 1151.
- 19 L. P. Olson, D. R. Whitcomb, M. Rajeswaran, T. N. Blanton and B. J. Stwertka, *Chem. Mater.*, 2006, **18**, 1667.
- 20 M. R. V. Sahyun, *J. Imaging Sci. Technol.*, 1998, **42**, 23.
- 21 L. Oshry and S. M. Rosenfeld, *Org. Prep. Proced. Int.*, 1982, **14**, 249.
- 22 K. Suganuma, S. Yamaguchi and M. Hatamura, WO2007/004437.
- 23 (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648; (b) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (d) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.
- 24 (a) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; (b) W. R. Wadt and P. J. Hay, *Chem. Phys.* 1985, **82**, 284; (c) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, **1985**, **82**, 299.
- 25 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2009.
- 26 T.A. Keith, *AIMAll* (Version 13.11.04), TK Gristmill Software, Overland Park KS, USA, 2013 (<http://aim.tkgristmill.com/>).
- 27 R. C. Krueger, *J. Am. Chem. Soc.*, 1952, **74**, 5536.
- 28 V. Logvinenko, O. Polunina, Y. Mikhailov, K. Mikhailov and B. Bokhonov, *Journal of Thermal Analysis and Calorimetry*, 2007, **90**, 813.
- 29 L. Du, W. Shi, L. Hou, Y. Wang, Q. Shi and Z. Zhu, *Inorg. Chem.* 2013, **52**, 14018.
- 30 V. N. Richards, N. P. Rath and W. E. Buhro, *Chem. Mater.*, 2010, **22**, 3556.

^a The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan.

^b Department of Information Systems Engineering, Osaka Sangyo University, 3-1-1 Nakakaito Daito, Osaka 574-8530, Japan.

* To whom correspondence should be addressed. For M.Hatamura: e-mail, hatamura@sanken.osaka-u.ac.jp

On and after retirement of M. Hatamura; 30th March 2015, to whom correspondence should be addressed. For S. Yamaguchi: e-mail, shunro@sanken.osaka-u.ac.jp

*Tel: +81-(0)6-6879-8473; Fax: +81-(0)6-6879-8522

Supporting Information.

¹³C-NMR data of Compounds 1a-8a

FT-IR data of Compounds 1a-8a

Dart Mass data of Compounds 1a-8a

GC Mass data of Compounds 7a-8a

TG data of Compound 1a-8a

DSC data of Compounds 1a-8a,

XRD data of Inorganic residue: Compounds 1b-8b

Cartesian coordinates of optimized structures

Table 3 Selected bond lengths and AIM properties at each BCP

