Coordination Chemistry of Photothermographic Imaging Materials: III

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Silver carboxylates have played a major role in thermographic and photothermographic technology since the introduction of these imaging materials in the 1950s. The nature of the bonding in these coordination compounds is sufficient to describe many of the properties needed by the silver source in order to function successfully in these imaging systems. Understanding the entire range of physical and chemical properties of silver carboxylates enables new silver sources possessing novel properties to be designed. This report describes our continuing efforts to elucidate the nature of the inorganic reaction chemistries occurring within the imaging construction, including silver-containing intermediates, such as disilver phthalate. In addition, based on the solid state structure of long chain silver carboxylates, we now report how the solid state properties of the silver carboxylates can be intentionally engineered to form novel, asymmetric silver carboxylate dimers, and what role those new materials could play in the imaging reactions based on these compounds.

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Introduction

Silver carboxylates have played a major role as the source of the silver ion for the metallic image in virtually all commercially available photothermographic (PTG) imaging materials.[1–3] The nature of the bonding in these silver carboxylate coordination compounds can be used to describe many of the properties needed by the silver source to function successfully in a photothermographic system in order to provide the silver ion for the development reaction but not for D_{min} formation. For example, the supramolecular architecture (the cross-coordination ability of certain ligands to generate molecular structures exceeding molecular boundaries) of silver carboxylates has been used to describe the silver coordination sphere in these materials[4] and its effect on controlling their reactivity properties. The properties of the silver source that are considered useful for PTG materials have been described in more detail previously.[1] Understanding the entire range of physical and chemical properties of silver carboxylates used in these imaging materials enables new silver sources possessing novel properties to be designed. We now report novel silver carboxylate asymmetric dimer structures and how they might affect imaging properties of materials built on them.

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Very little has been reported in the literature on the reactions occurring between the silver ions and the other imaging components.[5–7] This article is the third in a series of our continuing efforts[5,6] to elucidate the nature of the inorganic reaction chemistries occurring at various stages within the photothermographic construction. This work is focused on the silver-containing intermediates and how the solid state properties of the silver carboxylates might be designed to influence the course of those reactions.[8,9]

Previously, the reaction between the silver carboxylate and the common toners, phthalazine and phthalic acid (PHZ, H_2PA) (Fig. 1), was discussed in the first report.[5] The model compounds $[\{Ag(O_2CCH_3)(PHZ)(H_2O)_2\}_2]$ and $[Ag_2(PHZ)_2(PA)\cdot H_2O]$, in which the silver complexes contained both the carboxylate and phthalazine, were reported and characterized in detail, including the solid state crystal structures.[10,11] Also, for the first time, the solid state structure of silver stearate, a fundamental component or a model thereof in all contemporary PTG constructions, was reported in that first report. In the second report, the structural investigation of silver carboxylate reaction chemistries was continued.[6] Some of the complexes formed between the silver stearate and stabilizers, such as triphenylphosphine and mercaptobenizimidazole, as well as the formation of various co-toner complexes resulting from incorporation of PHZ and H_2PA components in the PTG system, were considered in detail.

Recently, disilver phthalate, Ag_2PA, has been reported as the primary silver-containing complex initially formed during the thermal development reaction[7] in PTG materials containing silver behenate, PHZ, and H_2PA. The proposal provides evidence for the extraction of silver

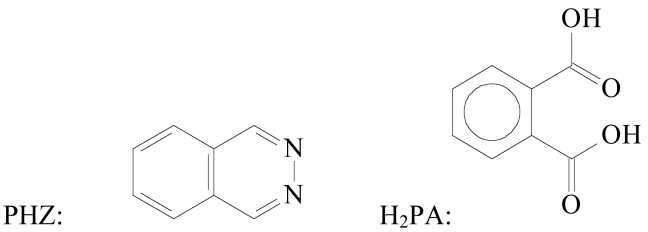

Figure 1. PHZ, H_2PA, respectively.

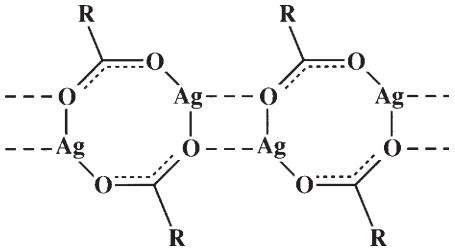

Figure 2. Eight-membered ring repeating unit in silver carboxylates.

ions from the silver soap lattice by the formation of Ag_2PA, which is then proposed to begin its journey through the development process. In order to shed more light on this proposal and provide a better understanding of the imaging chemistry occurring during development, we have undertaken an effort to prepare suitable crystals of Ag_2PA and determine its solid state structure. The results of this investigation, and the relationship of the Ag_2PA structure to imaging chemistry within PTG systems, are described below.

In addition, the unraveling of the solid state structure of silver stearate, a good model of the silver carboxylates used within all contemporary PTG imaging media,[12] has led to the rationale design of novel silver carboxylate compounds.[8,13] Because the silver carboxylates are dimeric, consisting of $[AgO_2CR]_2$ repeating units (Fig. 2), specific selection of varying the R groups enables asymmetric dimers to be prepared. By proper choice of carboxylate and selection of preparation conditions, novel silver carboxylate compounds can be prepared. More specifically, by intentional selection of R to be significantly different from R', novel solid state materials can be engineered.[9,13] A new proposal regarding development intermediates in the PTG imaging chemistry is provided by combining both the understanding of the solid state structure of Ag_2PA and the newly discovered asymmetric silver carboxylate dimers.

Experimental

Preparation of Compounds

Preparation of Ag_2PA: 0.34 g silver acetate and 0.15 g phthalic acid were dissolved in 80 mL hot H_2O. Filtration removed a slight amount of solid, and the clear, colorless filtrate was allowed to stand and slowly lose solvent. Extremely small, colorless crystals resulted.

Preparation of asymmetric silver carboxylates: Sodium hydroxide (20 mmol) was dissolved in water (150 mL) and heated above the Krafft temperature of the acids to be used. A slight excess of the stoichiometric amount of both acids, RCO_2H (10 mmol) and $R'CO_2H$ (10 mmol), relative to the base, was added with vigorous stirring. After 2 min, the mixed sodium soap solution was removed from the heat and, with stirring, allowed to cool below the Krafft temperature of the mixture. Silver nitrate (20 mmol) was added in 5 mL H_2O, and the mixture was stirred for 30 min. The white dispersion was filtered, redispersed in water, stirred, filtered, and allowed to dry at room temperature.

Instrumental

A thin plate crystal of Ag_2PA with approximate dimensions of 0.02 x 0.06 x 0.10 mm^3, was chosen for data collection. Diffraction data were collected at 100 °K using Nonius Kappa-CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). A total of 368 frames were collected using phi plus omega scans to fill the asymmetric unit with a scan range of 1.6° and a counting time of 90 sec per degree. The first 10 frames were used for indexing reflections using the DENZO package and refined to obtain final cell parameters. Data reductions were performed using DENZO-SMN.[14]

The $P2_1/c$ space group was uniquely determined from the space group absences. The structure was solved by direct methods and refined by full-matrix least squares on F^2 with anisotropic displacement parameters for the non-hydrogen atoms using Bruker, SHELXTL.[15] Details of the crystallographic data collection and refinement parameters are given in Table I. Selected bond distances and angles for Ag_2PA are listed in Table II.

The DSC data were collected on a TA Instruments DSC model 2930, dual sample cell, heated 10°C/min under nitrogen. Modulated DSC parameters: modulated temperature amplitude was ±0.080°C, and the modulation period was 60 sec with a heating rate of 0.5°C/min.

Mass spectral data were collected on an EXTREL FTMS Fourier transform mass spectrometer and a Kratos MS-50 triple sector mass spectrometer. For FAB, the sample was mixed with a viscous solvent (3-nitrobenzyl alcohol or glycerol) and exposed to Xenon atoms. The laser desorption mass spectra were obtained with a high-power, pulsed CO_2 (10.6 μ) laser: output of the laser was adjusted to ~0.05 J/pulse.

Results and Discussion

The solid state components of various portions of the PTG construction based on silver carboxylates remain interesting and have much to reveal. This study has two objectives: first, to describe the solid state structure of Ag_2PA and what that structure implies regarding its reactivity in PTG materials and, second, to describe the design and properties of novel asymmetric dimeric silver carboxylate compounds. Taking both of these objectives into account, new asymmetric silver carboxylate complexes containing phthalic acid and fatty acid as important intermediates in the thermal development reaction of imaging materials can be proposed.

Ag_2PA

A primary component of photothermographic (PTG) imaging materials is the toner, which enables the normally golden-brown color of Ag^0, formed from the thermally induced reduction of silver carboxylates, to be black. This color shift is critical for a commercially acceptable product. The toner combination that works exceptionally well in contemporary PTG constructions, PHZ and H_2PA, has been a favorite since its discovery 25 years ago.[16]

The role of PHZ and H_2PA and their derivatives in the PTG process has been explored and partially eluci-

TABLE I. Crystal Data and Structure Refinement for Ag_2PA*

Empirical formula	$C_{18}H_{12}Ag_4O_{10}$	
Formula weight	819.76	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.018(3) Å	α = 90°
	b = 12.832(3) Å	β = 102.69(3)°
	c = 11.094(2) Å	γ = 90°
Volume	1946.8(7) $Å^3$	
Z	4	
Density (calculated)	2.797 Mg/m^3	
Absorption coefficient	4.023 mm^{-1}	
F(000)	1552	
Crystal size	0.02 x 0.06 x 0.10 mm^3	
Theta range for data collection	2.46 to 25.32°.	
Index ranges	$-16 \le h \le 16, -15 \le k \le 13, -13 \le l \le 13$	
Reflections collected	15287	
Independent reflections	3507 [R(int) = 0.1264]	
Completeness to θ = 27.12°	98.5 %	
Absorption correction	Multiscan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3507 / 0 / 291	
Goodness-of-fit on F^2	0.954	
Final R indices [I>2σ(I)]	R1 = 0.0414, wR2 = 0.0769	
R indices (all data)	R1 = 0.0852, wR2 = 0.0878	
Largest diff. peak and hole	0.695 and –0.869 e.$Å^{-3}$	

*The Cambridge Crystallographic Data Center contains the supplemental crystallographic data for this structure, CCDC 193797. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

dated.[10,11] The primary conclusions in those reports were that the PHZ could readily extract the silver ion as silver carboxylate complexes, which may be reduced at the latent image sites. Recently, the very first step in the thermal development chemistry of PTG has been proposed to be the formation of Ag_2PA, Step (1), allowing the silver ion to be extracted from the insoluble silver soap:[7]

$$[Ag(O_2C_{22}H_{43})]_2 + H_2PA \rightarrow Ag_2PA + 2\ HO_2C_{22}H_{43} \quad (1)$$

Subsequent reactions, Steps (2) and (3) are proposed to deliver the silver ion to the latent image where development would occur, respectively:

$$Ag_2PA + PHZ \rightarrow [AgPHZ]^+ + [Ag(PHZ)_2]^+ \quad (2)$$

$$[AgPHZ]^+ + [Ag(PHZ)_2]^+ + \text{developer} \rightarrow 2Ag^0 + 2PHZ \quad (3)$$

If Ag_2PA is the primary, first intermediate, its solid state and solubility properties could be expected to play a major role in its contribution to the subsequent reactions. The solid state structure of Ag_2PA has now been resolved and some of the consequences of the structure on the imaging properties in a PTG construction are discussed below.

Structure of Ag_2PA

In order to understand the structure of disilver phthalate, it is useful to first briefly review the structures of related compounds. Surprisingly, the solid state structures of many simple silver carboxylates have not been reported, including silver acetate, disilver phthalate, and monosilver phthalate. In fact, it is significant to note that there are very few references referring to the

TABLE II. Selected Bond Lengths [Å] and Angles [°] for Ag_2PA.

Ag(1)–Ag(3)	2.9886(10)
Ag(2)–O(6)	2.176(5)
Ag(2)–Ag(4)	3.1401(10)
Ag(2)–Ag(3)	3.3721(10)
Ag(3)–O(7)	2.182(5)
Ag(3)–O(1)	2.185(5)
Ag(3)–Ag(4)	2.8370(11)
Ag(4)–O(2)	2.244(5)
Ag(4)–O(8)	2.330(5)
Ag(4)–O(10)	2.538(5)
O(6)–Ag(2)–Ag(4)	108.63(14)
O(6)–Ag(2)–Ag(3)	60.79(14)
Ag(4)–Ag(2)–Ag(3)	51.50(2)
O(7)–Ag(3)–O(1)	166.44(17)
O(7)–Ag(3)–Ag(4)	80.59(13)
O(1)–Ag(3)–Ag(4)	86.04(12)
O(7)–Ag(3)–Ag(1)	73.57(13)
O(1)–Ag(3)–Ag(1)	108.40(13)
Ag(4)–Ag(3)–Ag(1)	88.02(2)
O(7)–Ag(3)–Ag(2)	83.59(13)
O(1)–Ag(3)–Ag(2)	87.80(13)
Ag(4)–Ag(3)–Ag(2)	60.03(2)
Ag(1)–Ag(3)–Ag(2)	143.56(3)
O(2)–Ag(4)–O(8)	148.46(18)
O(2)–Ag(4)–O(10)	88.80(18)
O(8)–Ag(4)–O(10)	106.38(17)
O(2)–Ag(4)–Ag(3)	77.53(13)
O(8)–Ag(4)–Ag(3)	77.76(12)
O(10)–Ag(4)–Ag(3)	155.49(12)
O(2)–Ag(4)–Ag(2)	92.98(14)
O(8)–Ag(4)–Ag(2)	59.64(11)
O(10)–Ag(4)–Ag(2)	92.38(13)
Ag(3)–Ag(4)–Ag(2)	68.47(2)

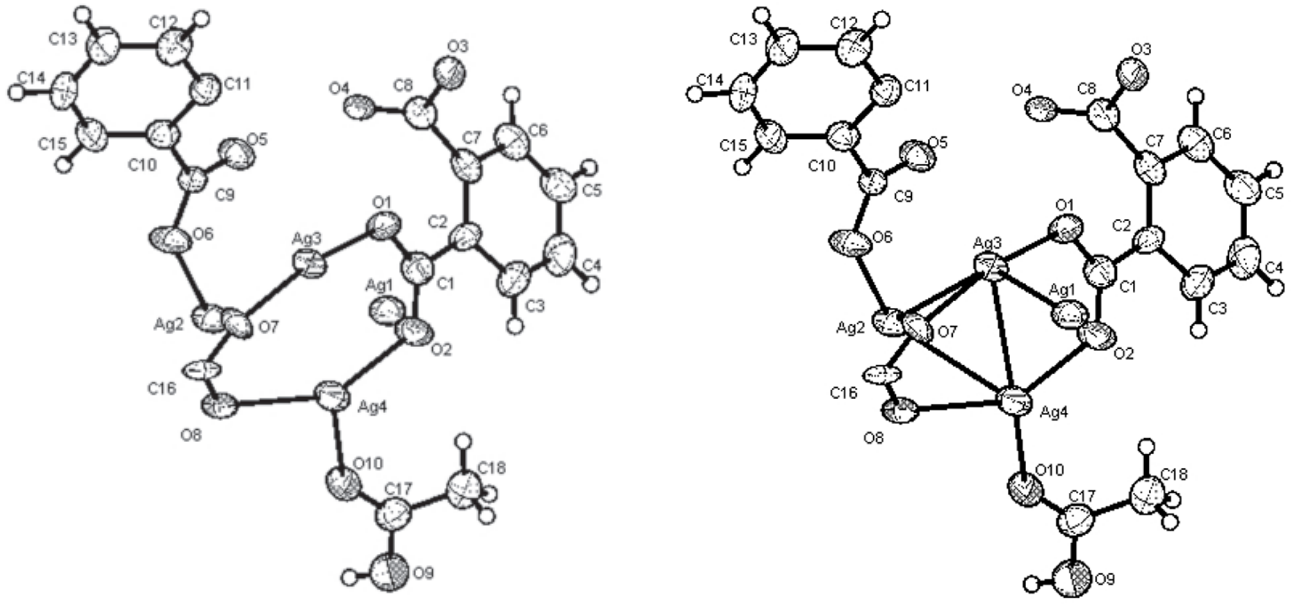

Figure 3. Structure of Ag_2PA showing 50% probability displacement ellipsoids and the atomic numbering scheme.

preparation of either disilver phthalate or monosilver phthalate. Normally, only a cursory note seems to be included in such references, without details.[17] There is only one significant exception that clearly describes the procedure used for the preparation of Ag_2PA as well as elemental analysis confirmation of the result.[7]

The solid state structure of various silver carboxylates such as silver benzoates,[18,19] silver oxalate,[20,21] and silver stearate,[12] have been reported. The fundamental bonding mode of the carboxylate in silver carboxylates has been identified[22–24] and these latter reports, and references cited therein, fit the pattern. First and foremost, as noted above, the carboxylate always bridges two silver atoms (unless other potential coordinating groups are available to bond to silver, such as in alpha-substituted carboxylates[8]). It is also significant that the silver ion in all such "simple" silver carboxylates is further coordinated by weaker, Ag···O bonds.[1,4]

While the structure of Ag_2PA has not previously been reported, the pyridine derivative has been reported. The structure is complicated and is comprised of three ring systems: a four membered Ag-O-Ag-O ring, a four-membered Ag-O-C-O chelate ring, and a seven-membered Ag-O-C-(benzene)-C-O chelate ring.[25] The ability of the phthalic acid in this case to bond to multiple silver sites provides many opportunities to cross-link in the solid. The phthalazine analog has also been reported.[10] In this case, the carboxylates are again involved in a polymeric structure. In addition, the ammine version of Ag_2PA has been reported.[26] Unlike the pyridine version, however, the ammine prevents the carboxylate from bridging the silver atoms and a linear complex results.

The pyridine version of silver benzoate, $[Ag_2(pyridine)_2(benzoate)_2]$, has also been reported. This complex is in the form of a polymeric lattice that is formed from the four-membered Ag-O-Ag-O ring acting as a bridge between the eight-membered Ag-O-C-O-Ag-O-C-O dimeric units.[27] The polymeric chains found in this complex have some resemblance to those in the $\{[Ag(PHZ)(O_2CCH_3)(H_2O)_2]_2\}_n$ complex.[11] In contrast to the phthalic acid complex noted above, the Ag-Ag separations in this complex are 2.85 and 2.90 Å (Table II), easily within the range considered significant for metal–metal interaction.

With this background, it is easier to put the structure of Ag_2PA into perspective. The solid state structure of Ag_2PA itself, however, is extremely complicated. Because of the overlapping bonding scheme in this complex, it is difficult to clearly display it in a static 2D format, thus various viewing angles are given below. A cif file is available as **Supplemental Material** from the IS&T website for 3D viewing. An ORTEP view of crystal structure of Ag_2PA with the atom labeling scheme is given in Fig. 3.[28]

There are two different silver carboxylate eight membered rings. One is very planar, as is normal, while the other is distorted. The two eight membered silver carboxylate rings lie approximately flat over each other, twisted 63.7°. Consequently, the silver-oxygen bonding results in a 4-coordinate silver (5-coordinate silver, if the Ag-Ag separation is considered bonding). This enhanced bonding, compared to 3-coordinate silver in most silver carboxylates, can be expected to affect the physical and chemical properties of the solid state. One stereo view of two such ring systems is given in Fig. 4.

It should be noted, however, that the two eight membered silver carboxylate rings are not the same, as one is quite flat and the other rather distorted from planarity. The distorted ring shows additional connections.

The Ag_2PA repeating unit creates a layered structure interspersed with acetic acid, which is weakly coordinated to a silver, Ag-O = 2.538(5) Å. While difficult to view in two dimensions, the layers can be seen very distinctly in three dimensions. Each layer is highly cross-linked with $[AgO_2CR]_2$ dimer fragments linked together by longer, $Ag\cdots O_{\text{neighboring dimer}}$ bonding connections. These bonding connections guarantee, among other things, extremely poor solubility and explain why obtaining a good quality crystal for structure determination is difficult.

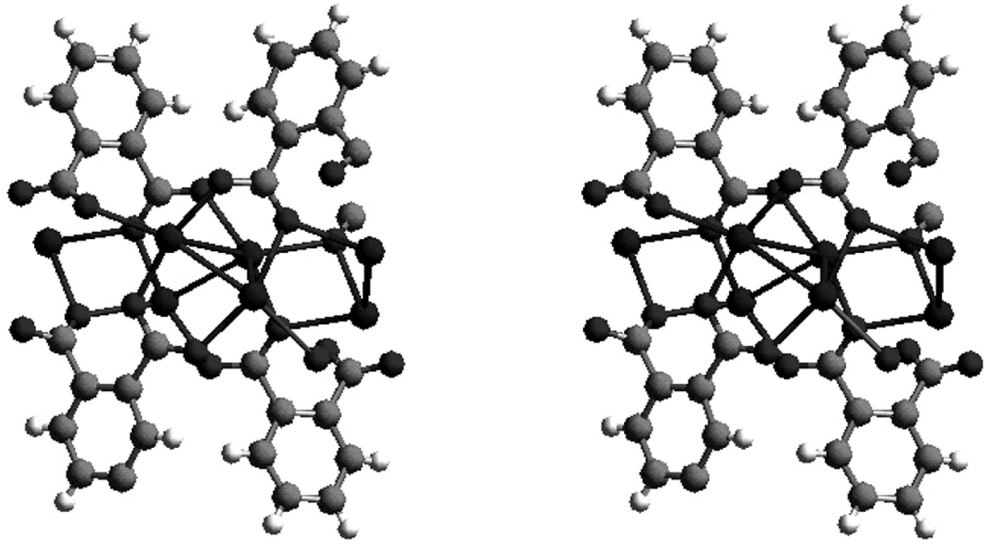

Figure 4. Stereo view of the two eight-membered silver carboxylate ring fragment of the Ag_2PA unit cell.

Implications of the Ag_2PA Structure on Imaging in PTG

As can be seen from the solid state structure shown above, the proposed Ag_2PA as an intermediate in the PTG development reaction needs to be rationalized. In addition, the subsequent steps involve the formation of $[Ag\text{-}PHZ]^+$ and $[Ag_2\text{-}PHZ]^{2+}$ intermediates, which are proposed to be the silver-containing compounds that are eventually reduced at the latent image sites. Other potential intermediates reported previously, such as $[Ag_2(PHZ)_2(PA)\cdot H_2O]$, were not considered in this scheme.

The poor solubility of Ag_2PA in non-coordinating solvents (including water) can be readily understood from the solid state structure. The highly cross-linked nature of the Ag_2PA complex can be expected to prevent facile solubility, particularly in comparison to the silver soap. Consequently, it is difficult to imagine Ag_2PA as a mobile, silver-transport complex.

Occasionally, thermal transitions such as melting points have been considered important in the development chemistry of thermally active systems.[3] This mechanism, however, cannot be invoked here, as Ag_2PA shows no thermal transitions below 200°C; the DSC shows only a flat baseline. Again, this thermal inertness can be attributed directly to the highly cross-linked silver carboxylates in the solid state structure of the Ag_2PA.

Also, Ag_2PA is thermally inert with the developer at 122°C. Higher temperature is needed to force the formation of Ag^0 (100% of the Ag_2PA develops near 130°C). This "inertness" can be attributed to its highly cross-linked structure, particularly when compared to silver stearate, which is less cross-linked and reacts thermally with the developer at lower temperatures.

The other possible silver phthalate complex, mono silver phthalate, Ag-H-PA, might be considered as more likely than Ag_2PA, if one wants to provide a phthalate-containing, silver complex intermediate. To our knowledge, this complex has never been reported in the literature. In our hands, all attempts to prepare Ag-H-PA have resulted in Ag_2PA only.

Conclusions Based on the Solid State Structure of Ag_2PA

We have found that the solid state structure of Ag_2PA consists of silver carboxylate eight membered ring dimers that are intricately connected together to form a highly crosslinked, inert solid. The structure provides a basis for understanding the physical and chemical properties of the Ag_2PA and suggests that it is unlikely the primary intermediate in the development chemistry of PTG materials. While H_2PA is a significant component in the imaging chemistry, a critically different role is proposed, as described below.

Asymmetric Silver Carboxylates

As noted above, all simple silver carboxylate complexes are constructed around an eight membered $[AgO_2C]_2$ core. The additional, longer Ag···O bond between the silver carboxylate dimers create the polymeric solid state structure seen in all silver carboxylate compounds. As long as a single carboxylate is used in the preparation step, a symmetric silver carboxylate structure will result. Mixing carboxylates, however, provides the conditions for the preparation of a new type of structure, the asymmetric dimer, where R and R' are present in the same dimer.

One of the best methods to detect the asymmetric dimer in the solid state is *via* X-ray diffraction, ideally by crystal structure determination, but also from powder data. The latter are particularly important in preliminary screening because the structure is easily detected in a material having a highly diffracting, layered structure such as silver carboxylates.

The separation between the silver layers, the d_{layer} spacing, is approximately the length of the two hydrocarbon chains. For silver palmitate, AgPa, C_{16}, for example, this is well known to be 43.66 Å[29] and it is 58.9 Å for silver behenate, AgBe, C_{22}.[30] If, however, the two chain lengths were mixed together, a new single-phase, asymmetric silver carboxylate in the solid state could be expected. In this case, the d_{layer} spacing for the asymmetric complex of PaAgAgBe, $C_{16}AgAgC_{22}$, should be equivalent to the d_{layer} spacing of the average chain

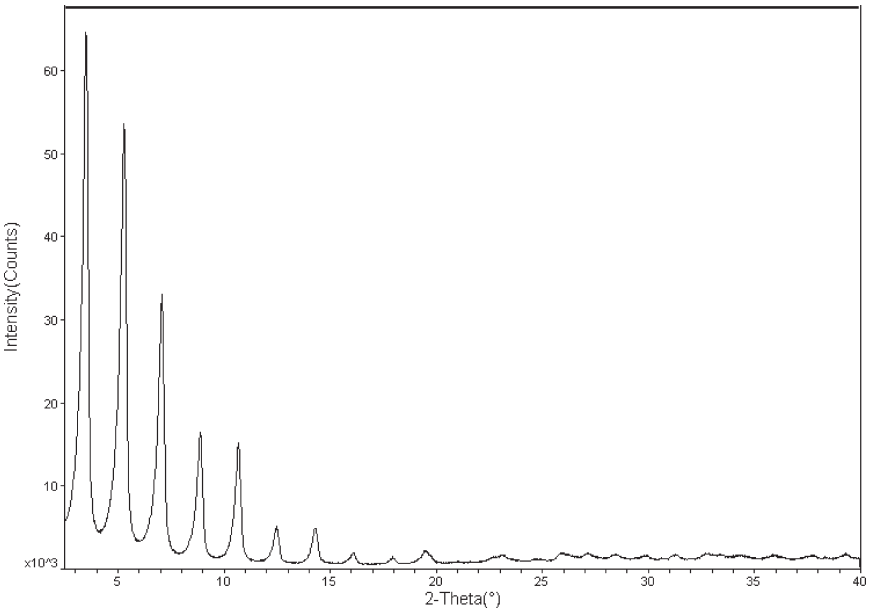

Figure 5. X-ray diffraction pattern of PaAgAgBe.

TABLE III. Selected d_{layer} Spacings in Asymmetric Silver Carboxylates, RAgAgR'

R	R'	(R+R')/2	d_{001} – calculated[a]	d_{001} – found
22	28	25	66.05	66.6
14	20	17	47.01	46.4
15	24	19.5	52.96	52.8
14	22	18	49.39	48.8
16	23	19.5	52.96	52.9
12	22	17	47.01	48.8
16	22	19	51.77	51.3
15	21	18	49.39	49.4

a: d(Å) = 6.55 + 2.38 (R+R')/2[30]

length, $C_{19}AgAgC_{19}$. Thus, using an empirical equation for measuring the d_{layer} spacing,[30] the theoretical d_{layer} spacing for the symmetric silver nonadecanoate is 51.77 Å, 51.3 Å was found. The X-ray diffraction pattern for the latter is shown in Fig. 5.

This diffraction pattern is also remarkable in that the silver complex is cleanly a single-phase material. There is no indication of either the AgPa or AgBe symmetric phases as impurities. Under the conditions of the experiment, one might have expected a 1:2:1 ratio of AgPa:PaAgAgBe:AgBe, but there is very little sign of the other two phases.

The X-ray pattern shown above is not unique to this pair of chain lengths. A broad series of chain lengths, not limited to a six-carbon separation, has been prepared. Nearly all the silver complexes are more than 98% single phase, asymmetric dimers, regardless of the number of carbons in different lengths. Even the cases where odd chain lengths are used, either as pairs or mixed with the even chain lengths, the same X-ray patterns characteristic of the asymmetric dimers were observed. Only the longest difference, ten carbons, showed any significant deviation from the expected d_{layer} spacing. Some of these results are shown in Table III.

Considering the significant differences in the chain lengths in the asymmetric dimers, one could expect correspondingly significant differences in the solid state properties. This is precisely observed. For example, in Fig. 6 three DSCs are shown, one each for the pure symmetric dimers of AgBe and AgPa, and the third is the thermal phase behavior of the mixed asymmetric dimer, PaAgAgBe.

It is clear that, like the X-ray diffraction results, there is no indication of the presence of either symmetric dimer. Furthermore, the new phase transitions observed are quite different, both in number and temperature, than the parents. The same trends, both in the X-ray diffraction and DSC results, are observed with the entire series of asymmetric silver carboxylates shown above. The impact on the mechanism of the development process in thermographic systems, based on silver carboxylates and toner systems, can be explored. For the reaction involving phthalic acid, a series of laser desorption mass spectra data was obtained, as seen in Table IV.

One of the key advantages of mass spectra data is that the ^{107}Ag and ^{109}Ag isotopes, at approximately 1:1 ratio, can be used to definitively assign peaks that contain silver. Under these circumstances, various fragments of AgSt and AgPHZ are observed, similar to that reported by Maekawa.[7] In addition, however, the most significant set of peaks can be assigned to the fragmentation pattern for an asymmetric dimer comprised of stearate and phthalate. The StAgAgPA dimer is entirely consistent with the proposed intermediate in the thermal development reaction, as it would be expected to exhibit better solubility and, therefore, better thermal transport properties. The specific complex proposed is shown in Fig. 7.

It might be noted that, while these complexes are the first asymmetric silver carboxylates to be reported, asymmetric metal carboxylates are not unknown, although they are not common. To our knowledge, the first report of an asymmetric metal carboxylate complex was reported in 1992 and was based on cadmium complexes

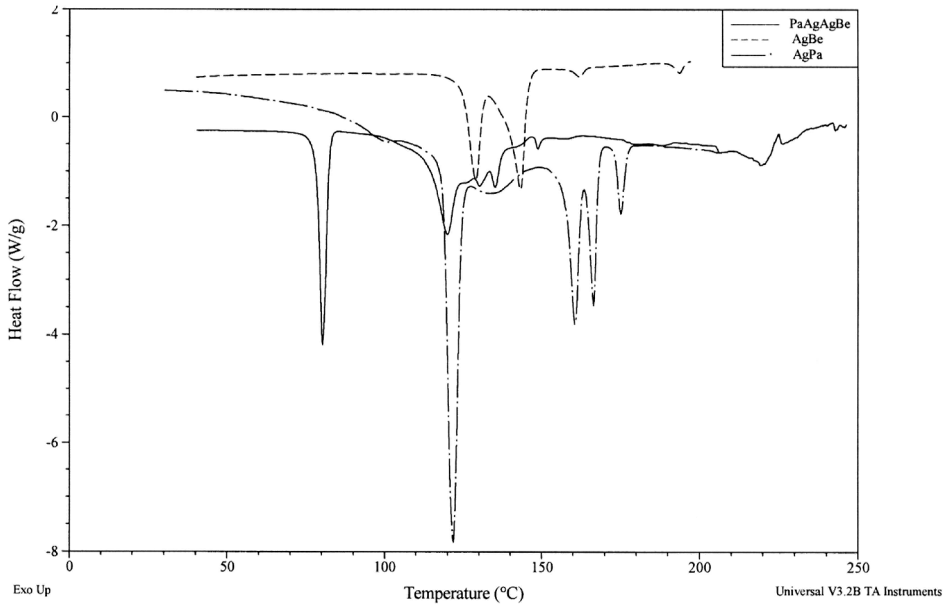

Figure 6. DSC of AgPa, AgBe and the asymmetric dimer, PaAgAgBe.

TABLE IV. Laser Desorption of AgSt + H_2PA + PHZ

	Positive ion LD		Negative ion LD	
Sample	Species	*m/z*	Species	*m/z*
A	Ag	107/109	PA	165
	PHZ	130	St	283
	Ag-PHZ	237/239		
	Ag-PHZ_2	367/369		
	Ag-St	391/393		
B	PHZ	130	St	283
	Ag-PHZ	237/239	Ag-St_2	673/675
	Ag-St	391/393	AgSt(PA-$2CO_2$)	467 cluster
	Ag_2-St	497/499/501		
			AgSt(PA-CO_2)	512 cluster
AgSt	Ag-St	391/393	St	283
	Ag_2-St	497/499/501		

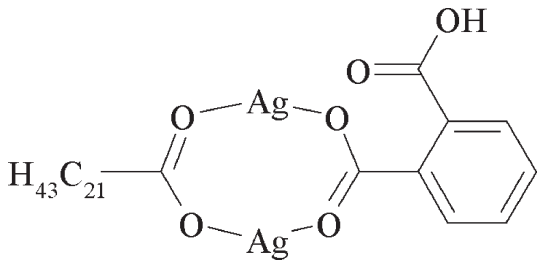

Figure 7. Proposed structure of the asymmetric silver carboxylate dimer formed in the thermal development reaction of PTG systems containing silver carboxylate and phthalic acid toner.

of stearic and behenic acids.[31] Using a 1:1 Be:St ratio, the X-ray diffraction data of Langmuir–Blodgett films clearly showed the layer spacing expected for the asymmetric dimer and was equivalent to the chain length of the intermediate acid, arachidic.

In 2001, a new asymmetric metal carboxylate was reported with manganese[32] in which the mixed carboxylates provided significantly different properties to the resulting asymmetric complexes. In this case, $[Mn_{12}O_{12}(O_2CR)_8\text{-}(O_2CR')_8(H_2O)_3]$ complexes were found to not only exhibit very different solubility properties compared to the starting symmetric carboxylate, but also to exhibit modified redox properties.

Conclusions

Taking the properties of the newly prepared, asymmetric metal complexes into account, the differences in the solid state properties of the symmetric vs asymmetric metal carboxylates, the solid state properties of Ag_2PA, the ability of H_2PA to extract silver from AgBe, and the stoichiometry of TG and PTG imaging constructions based on silver carboxylates, the StAgAgPA asymmetric dimer is proposed as one of the main components of the silver ion transport compound in the development process of thermographic materials.

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