

Silver Coordination Chemistry of Photothermographic Imaging Systems, IV

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Abstract

Photothermographic (PTG) imaging materials have become an indispensable application of silver technology that capitalizes on the 1-electron reduction capability of silver to form a black and white image. Metallic silver, the light-absorbing component of these imaging materials, has a unique morphology that provides good optical density and image tone. Understanding the silver chemistry portion of the metallic image formation process is important toward improving the photographic response of these materials. We have continued our investigation of various aspects of the silver coordination chemistry and report the solid-state structures of several silver complexes, utilizing ligands present in the PTG formulation, as well as model structures. Depending on the complexing agent and silver counterion, various silver complexes can be isolated and characterized. This report illustrates the silver-ligand interactions and characterizes the new compounds formed, as well as what role the ligand functionality could play in the imaging reactions based on these compounds.

Introduction

Photothermographic (PTG) technology, based on silver carboxylates^{1,2} and the commercially successful products constructed from them, celebrates its 40th anniversary in 2004. The invention of 3M dry silver paper, first introduced in 1964,³ heralded the beginning of a new method of simply obtaining a black and white image. Light exposure, followed by a short, dry development (120 °C, 15 s) produced a useful black and white imaging material. The fact that this process did not need complicated and messy wet processing of conventional silver halide photographic materials was not lost on the customer who made this product a success. This latter point is illustrated when it is realized that now, over 30,000 Kodak DryView laser imaging systems have been placed in the medical market since 1995.

Despite the commercial significance of this technology, past and present, compared to conventional silver halide-based black and white imaging, surprisingly little understanding of the PTG process has been published.⁴⁻¹⁰ In addition, the technology fundamental to the formation of the black and white image, the metallic silver particle, is still only partially understood.¹¹⁻¹⁴ This latter point is not surprising because PTG is not a simple process, as indicated by the different silver particle morphologies observed in different imaging formulations. Nevertheless, improvements should be possible as the principles underlying each stage of the PTG process are revealed. We discuss some of the silver coordination chemistry that may be participating in the overall silver-ion transport process and how that may contribute to the formation of the resulting metallic silver.

Results and Discussion

Most PTG formulations contain two important compounds that can form stable complexes with silver, phthalazine (PHZ) and phthalic acid (PA),^{9,10} Fig. 1, or their derivatives.

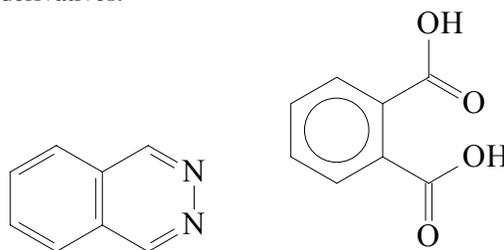


Figure 1. Phthalazine and phthalic acid

Considering how useful these compounds are in providing a suitably black image tone, some work has been published about trying to understand the role of these compounds in the imaging process. Previously, we showed the solid-state structures of Ag₂PA, AgPHZ-Ac, and AgPHZ-PA, and considered how their physical and chemical properties could contribute to the formation of

the metallic silver in the image. While each compound has been suggested as an important silver complexing agent,⁶ the solid-state properties are not consistent with the corresponding silver complex being significantly involved. Our efforts, recently, have been to adjust the coordination sphere around the silver using PA-based derivatives to reveal the important role of the ortho-dicarboxylic acids in this imaging process. We have now prepared silver complexes (from the aqueous solutions) of three members of this series, phthalic acid, monomethylphthalic acid (MPA), and *o*-acetyl-benzoic acid (Ac-BA), Fig. 2.

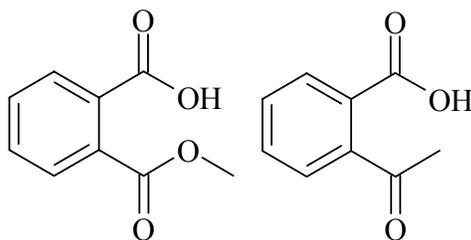


Figure 2. Mono-methylphthalic acid, *o*-acetyl-benzoic acid

A full description of the structures is not possible here, but from a solid-state structure perspective, all three complexes can be seen to be built upon the same 8-membered silver carboxylate dimeric ring fragment that is common to silver carboxylate frameworks. The carbonyl group of the *o*-substituted component, in all cases, also participates in bonding to silver. A schematic of the building block of each complex is shown in Fig. 3.

The fundamental difference between Ag_2PA and the Ag-AcBA and AgM-PA complexes is the inability of the latter to incorporate additional silver atoms into the structure, thereby lessening the intermolecular bonding between adjacent silver and acid groups. The practical consequence of this difference is that the weaker $\text{Ag-O}_{\text{carbonyl}}$ bonding link is susceptible to hydrolysis, enabling the complexes to exhibit water solubility not possible with Ag_2PA .

In order to fully explore the nature of the ortho-dicarboxylic acid system, a series of compounds were selected for incorporation into a PTG construction, the above-mentioned *cis*- and *trans*-cyclohexane dicarboxylic acid, and tetrachlorophthalic acid. Interestingly, only the PA provides sufficient reactivity for image formation. The results of this structure analysis and correlation to the film results suggest additional factors that must be taken into account when designing suitable toners for these types of formulations.

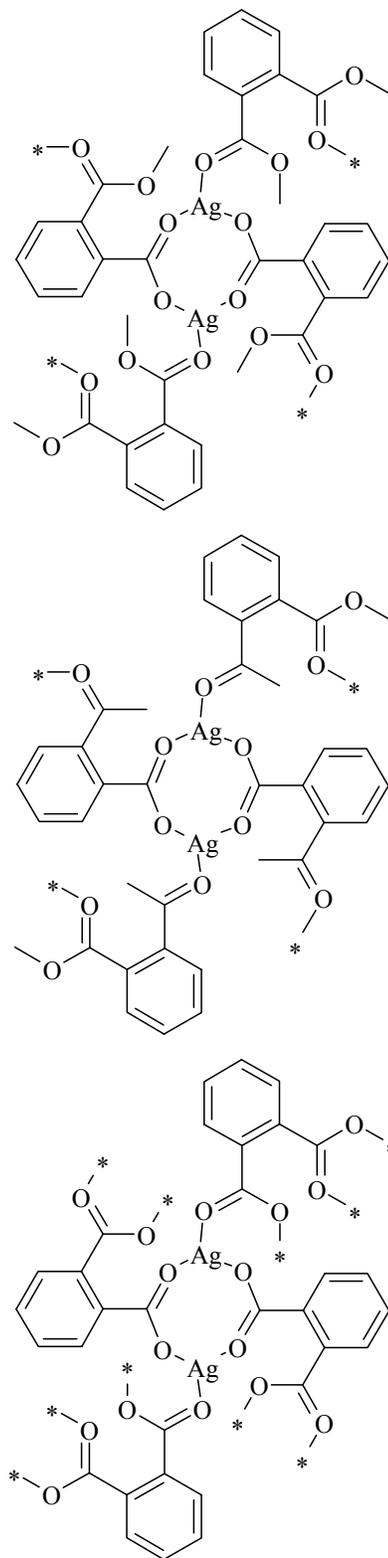


Figure 3. Schematic of AgMPA (top), AgAc-BA (middle), Ag_2PA (bottom), * = coordination link to Ag^+

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