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Silver Coordination Chemistry of Photothermographic Imaging Systems, IV

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Photothermographic (PTG) imaging materials have become an indispensable application of silver technology that capitalizes on the capability of silver to undergo reduction 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 new 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 of silver compounds based on ortho-dicarboxylic acids, as well as the role ligand functionality could play in the imaging reactions based on these compounds.

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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 high quality capability of the photothermographic process has been instrumental in its application to medical X-ray diagnostic film materials, such as DryView™, an important product for Eastman Kodak Company. The facts that this process did not introduce the complicated and hazardous waste disposal issues raised by wet processing of conventional silver halide photographic materials was not lost on the customers who have made this product a success. This latter point is illustrated when it is realized now that over 30,000 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.[4–12] In addition, the technology fundamental to the formation of the black and white image, the metallic silver particle, is still only partially understood.[13–16] This latter point is not surprising because PTG is not a simple system, 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. The objective of this work is to continue to reveal the silver coordination chemistry that is involved in the overall silver ion transport process and how that may contribute to the formation of the resulting metallic silver. Here, we focus on the silver chemistry of derivatives of phthalic acid, historically one of the key toners (silver complexing agents that modify image tone) in the photothermographic imaging formulation, which is currently used in all commercially available films. We find that the ortho-di-carboxylic aromatic acid structure is a critical feature of the toner, which is difficult to manipulate without adversely affecting imaging properties of the films.

Experimental

Preparation of Complexes

AgBDME. In 100 ml H_2O, 1.79 g 1,2-benzenedicarboxylic acid, monomethyl ester (BDME) and 0.37 g NaOH dissolved to form a clear solution. Addition of 1.70 g $AgNO_3$ in 5 ml H_2O yielded a completely colorless, clear solution. Slow evaporation to approximately half the volume produced thin, flaky, needle-like colorless needle crystals suitable for single-crystal X-ray diffraction.

AgAc–BA. In 50 ml H_2O, 1.65 g acetylbenzoic acid (*Ac–BA*) and 0.37g NaOH dissolved to form a clear solution. Addition of 1.70 g $AgNO_3$ in 5 ml H_2O produced a white

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solid, which after 30 min of stirring, was collected and air dried. A portion of the solid, 0.4 g, was redissolved in warmed 10 ml H_2O. Upon slow cooling, large, colorless blocks crystallized, suitable for single-crystal X-ray diffraction.

The crystal structure resolution and solid state structure details for these two complexes are reported separately.[17]

Preparation of Films

The PTG imaging formulation was prepared as generally described elsewhere.[18] The formulation contains silver carboxylates, preformed and in situ silver bromide, phthalic acid (PA), PHZ, along with the usual remaining components. When PA acid replacements were used, they were added as molar equivalents of PA at the same point during preparation. All materials were exposed at similar conditions with a scanning laser sensitometer incorporating an 811 nm laser diode. The samples were developed using a heated roll processor for 15 s at 122°C.

Results and Discussion

Photothermographic imaging materials, based on silver carboxylates and silver halides require, at a minimum, a developer (an electron source), a toner, and a binder.[1,2] Additional components, such as sensitizing dyes, stabilizers, etc., must also be included to improve overall photographic properties; these however, these are not considered here. The fundamental reactions are given below:

(1) $AgX + \text{light} \rightarrow AgX_{\text{latent image}}$

(2) $AgX_{\text{latent image}} + [Ag(O_2C_nH_{2n-1})]_2 + \text{developer/toner} + \text{heat} \rightarrow \text{intermediates} \rightarrow Ag^0_{\text{image}} + HO_2C_nH_{2n-1} + \text{oxidized developer/toner}$

It is the portion between the arrows, labeled "intermediates," that is of interest to us here. A key step in the mechanism of the PTG image development process for the silver source is for Ag^+ to be delivered to the $AgX_{\text{latent image}}$ where the reduction to elemental silver occurs. For optimum silver covering power and tone, the proper "toner" must be selected, although the role of the toner historically has generically been invoked in multiple important functions during the thermal development process. Not discussed in the literature of toner chemistry, for example, is that the toner can play up to four chemical roles in the eventual formation of image silver. That is, the toner can:

1. extract Ag^+ from the silver source;
2. transport Ag^+ from the insoluble/immobile silver source to the development sites via "intermediates" of silver complexes;
3. modify the redox potential of the Ag^+ via its structure as a new silver complex, which facilitates reduction with developer; and
4. adsorb to the growing silver surface, modifying the deposition of the next Ag^0 atom, and thereby affecting silver nanoparticle size and morphology

Strictly speaking, the name "toner" implies that it only affects the silver particle growth process, note 4, above, but extraction, transport, and redox modification can all be involved with various toners currently employed in PTG systems. Most commercial PTG formulations contain two important compounds that can form stable complexes with silver, phthalazine (PHZ) and phthalic acid (PA),[9,10] or their derivatives, see Fig. 1.

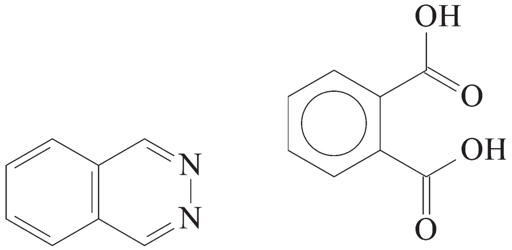

Figure 1. Phthalazine and phthalic acid.

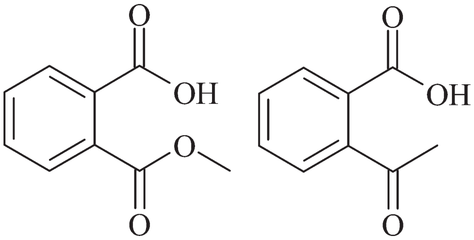

Figure 2. 1,2-Benzene-dicarboxylic acid, monomethyl ester, *o*-acetyl-benzoic acid.

It should be noted that, when in situ AgBr is utilized in a PTG construction, toners have been recently claimed to affect the PTG sensitivity by involvement with the process of in situ AgBr formation. This would fall into a category best labelled as a subset of role 1, above, since silver-toner complex intermediates are formed.[11,12] In these investigations, the phthalic acid isomers (*o*-, *m*- and *p*- carboxylate positions) and various amides (phthalimide, succinimide, phthalic acid di-amide, etc) were investigated. It was concluded that specific silver-toner complexes were formed as intermediates in the in situ preparation of AgBr crystallites. Under these circumstances the phthalimides were most effective in enhancing the photosensitivity of photopapers that were based on in situ AgBr sensitivity centers.

In contemporary PTG films, phthalic acid (H_2PA) and phthalazine (PHZ) have been used as "co-toners" although much remains to be learned regarding exactly how and precisely which of the above roles they play in the thermal development process. 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 resolved the solid state structures of $[AgPHZ\text{-}Ac]_2$,[19] and $[(AgPHZ)_2PA]$,[20] 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] and the phthalazine/carboxylic acid silver complexes show greatly enhanced reactivity with developers, the solid state properties of the pure silver carboxylate complexes are not consistent with that silver complex being involved significantly in the transport role of the toner. 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 and structurally characterized silver complexes of three members of this series, phthalic acid, 1,2-benzenedicarboxylic acid, monomethyl ester (BDME), and *o*-acetyl-benzoic acid (Ac-BA), Fig. 2.

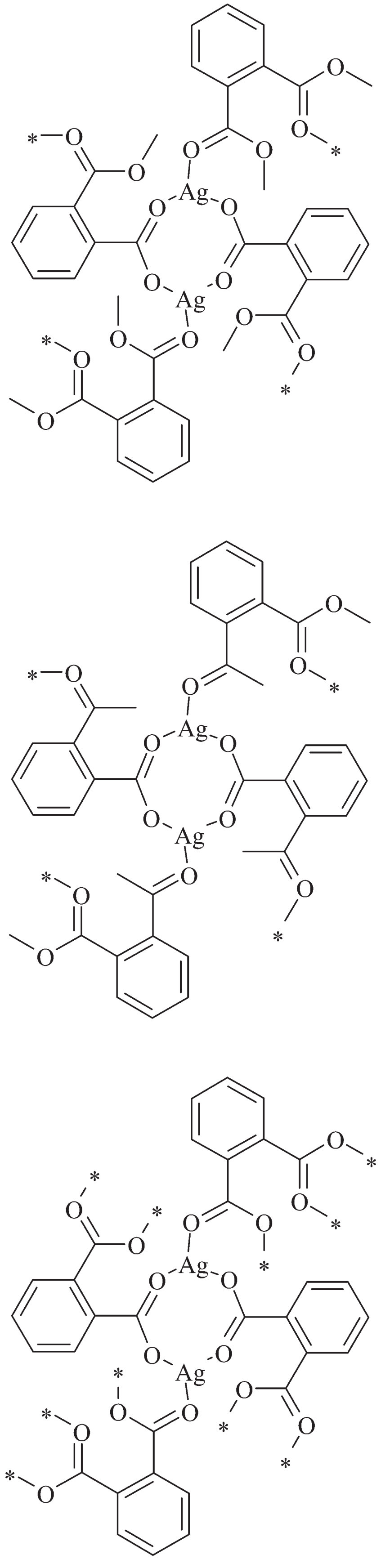

Figure 3. Schematic of AgBDME (top), AgAc–BA (middle), Ag$_2$PA (bottom), * = coordination link to Ag$^+$.

A full description of the structures of silver complexes prepared from these ligands is reported elsewhere,[10,17] 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$_2$PA and the Ag–AcBA and AgBDME 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 Ag–O$_{carbonyl}$ bonding link is susceptible to hydrolysis, enabling the complexes to exhibit water solubility not possible with Ag$_2$PA. From a PTG imaging point of view, this suggests that these ligands should promote more facile silver ion transport, if they react as described in role 2 above, on the assumption that the higher solubility translates to higher diffusion rates within the coated film. Some form of soluble silver complex must be forming with PA, at least, since no unassigned solid state products could be detected within the film during the imaging process.[21] When used in PTG material, however, only the PA toner provides sufficient reactivity for image formation. There is no image, that is Dmax = Dmin, for all of these acids but PA. Since Ag$_2$PA is more highly crosslinked than AgSt,[10] an Ag$_2$PA intermediate in the imaging process[6,7] is unlikely (and not detected[21]). More likely are asymmetric silver carboxylate dimers, LAgAgL’, which do not fit either the AgL or AgL’ lattice and thereby are more mobile during development.[10] While this type of complex has been reported for other metals,[22–24] we have not been able to obtain suitable crystals of the silver versions for X-ray diffraction characterization.

In order to further probe the nature of the ortho-di-carboxylic acid system, additional di-carboxylic acids were selected for incorporation into a PTG construction. The acids were selected for similar carboxylate configuration: *cis*- and *trans*-cyclohexane dicarboxylic acid, hemimellitic acid, *cis*-4-cyclohexene-1,2-dicarboxylic acid, and maleic acid, Fig. 4.

Similar to the Ac–BA and BDME cases, all these compounds, when used in place of phthalic acid in the PTG formulation, gave no image (Dmin = Dmax = 0.2). By comparison, the average image density for materials with PA is about 3.8.

Assuming that these ligands all extract silver ion from the silver behenate to approximately the same extent (role 1), we expect that the higher solubility of the Ac–BA and BDME silver complexes should eliminate silver ion transport (role 2) as a limiting factor in their reactivity. Therefore, these results suggest that the corresponding redox properties of the intermediate silver complex being delivered to the latent image site insufficiently match those of the developer being used (role 3). Without a metallic silver image to analyze, however, not much can be said about the potential of these compounds to modify metallic silver morphology (role 4).

There are additional possibilities, such as improper concentration optimization for each carboxylic acid. However, the results of this structure analysis (structures close to the PA structure) and correlation to the film results (from a good image with PA to no image for the other PA replacements discussed above) are consistent with the pure silver PA complexes as unlikely

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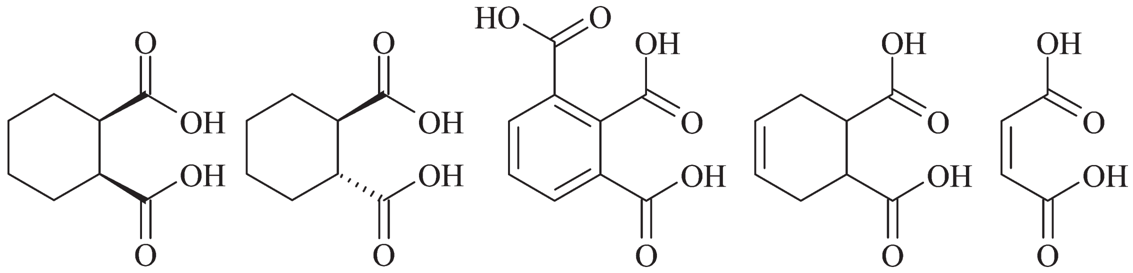

Figure 4. Structures for cis- and trans-cyclohexane di-carboxylic acid, hemimellitic, cis-4-cyclohexene-1,2-dicarboxylic acid, and maleic acid.

intermediates in the imaging process. Additional work is underway to better characterize those specific complexes and how they can be modified to improve the image forming process and to design better toners for these types of formulations.

Conclusions

New silver complexes of phthalic acid derivatives have been prepared and their solid state structures characterized. Incorporation of these derivatives and other ortho-di-carboxylic acid compounds as replacements for PA in the PTG formulation suggest that the pure silver carboxylate complexes are not the primary intermediates in the four potential roles the toner can play in the imaging chemisty: extraction, transportation, reduction, and toning of the metallic silver during the image forming process. Asymmetric silver complexes are more likely intermediates in this process, although more work must be undertaken to resolve this issue. The ortho-di-carboxylic aromatic acid structure is a critical feature of the toner, which is difficult to manipulate without adversely affecting imaging properties of the films. ▲

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References

1. P. J. Cowdery-Corvan and D. R. Whitcomb, *Handbook of Imaging Materials,* A. S. Diamond and D. S. Weiss, Eds., (Marcel Dekker, New York, NY, 2002), p. 473.
2. D. H. Klosterboer, *Neblette's Eighth Edition: Imaging Processes and Materials*, J. M. Sturge, V. Walworth, and A. Shepp, Eds., (Van Nostrand-Reinhold, New York, 1989), chap. 9, p. 279.
3. D. Morgan, BE Patent 663112 (1965).
4. M. R. V. Sahyun, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **42,** 23 (1998).
5. S. E. Hill, M. B. Mizen, M. R. V. Sahyun, and Yu. E. Usanov, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **40**, 568 (1996).
6. T. Maekawa, M. Yoshikane, H. Fujimura, and I. Toya, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **45**, 365 (2001).
7. H. L. Strijckers, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **47,** 100 (2003).
8. P. L. Potapov, D. Schryvers, H. Strijckers, and C. Van Roost, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **47,** 115 (2001).
9. D. R. Whitcomb and R. D. Rogers, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **43**, 517–520 (1999).
10. D. R. Whitcomb and M. Rajeswaran, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **47**, 107 (2003).
11. P. Z. Velinzon, S. I. Gaft, N. K. Ryasinskaya, and I. G. Chezlov, *Zhur. Nauch. i Priklad. Fotogr.* **47**(6), 11–21 (2002).
12. P. Z. Velinzon, S. I. Gaft, O. A. Karekina, N. K. Ryasinskaya, I. G. Chezlov, *Zhur. Nauch. i Priklad. Fotogr.* **48**(3), 35–45 (2003).
13. B. Bokhonov, L. Burleva, Yu. Usanov, and D. R. Whitcomb, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **45**, 259 (2003).
14. B. B. Bokhonov, L. P. Burleva, W. Frank, M. B. Mizen, M. R. V. Sahyun, D. R. Whitcomb, J. Winslow, and C. Zou, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **40**, 417 (1996).
15. B. B. Bokhonov, L. P. Burleva and D. R. Whitcomb, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **43**, 505–508 (1999).
16. B. B. Bokhonov, L. P. Burleva, Yu. E. Usanov, and D. R. Whitcomb, *Zh. Nauchn. Prikl. Fotogr.* **44**, 11 (1999).
17. D. R. Whitcomb and M. Rajeswaran, manuscript in preparation.
18. C. F. Zou, J. B. Philip, S. M. Shor, M. C. Skinner, and P. Zhou, U.S. Patent 5,434,043 (1995).
19. D. R. Whitcomb and R. D. Rogers, *J. Chem. Crystallogr.* **25**, 137 (1995).
20. D. R. Whitcomb and R. D. Rogers, *Inorg. Chim. Acta*, **256**, 263 (1997).
21. B. B. Bokhonov, M. R. Sharafutdinov, B. P. Tolochko, L. P. Burleva, and D. R. Whitcomb, *J. Imaging Sci. Technol.* ISSN: 1062-3701, **49**, 389 (2005).
22. W. Chen, J.-Y. Wang, C. Chen, Q. Yue, H.-M. Yuan, J.-S. Chen, and S.-N. Wang, *Inorg. Chem.* **42**, 944–946 (2003).
23. S. Dante, F. Rustichelli and V. Erokhin, *Mol. Cryst. Liq. Cryst.Sci. Technol.* **215**, 205 (1992).
24. M. Soler, P. Artus, K. Folting, J. C. Huffman, D. N. Hendrickson, and G. Christou, *Inorg. Chem.* **40**, 4902 (2001).