

# Applications of Gold Chemistry in Imaging Technology

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Gold compounds have played a critical role in imaging technology since the first report in 1925, that such compounds can sensitize silver halide emulsions to give significant increases in their photographic speed. Gold(3+) compounds, typically  $K[AuCl_4]$  or  $H[AuCl_4]$ , were first used as *chemical sensitizers* in commercial silver halide materials in the early 1940s. Such materials are added to the precipitated silver halide, dispersed in aqueous gelatin (historically, but incorrectly, called a silver halide “emulsion” rather than a dispersion), and form so-called “sensitization centers” on the surface of grains of the silver halide. Typically, the gold is added at a level of ca.  $10^{-5}$  mol/mol of AgX. Such sensitization, coupled with similar treatment with a labile sulfur compound, such as  $Na_2S_2O_3$  or a thiourea, to give S + Au chemical sensitization, has allowed the development of today’s high-speed photographic film. A problem associated with the use of such labile Au(3+) compounds is their facile reduction to Au(1+) by sulfur sites in gelatin and subsequent coordination to gelatin binding sites, significantly reducing the available gold for the sensitization function.

In the early 1990s, work was reported on the first successful introduction of stable Au(1+) coordination complexes as silver halide emulsion chemical sensitizers. The first of these new Au(I) chemical sensitizers was the linear, 2-coordinate cationic complex with a mesoionic thiolate,  $[Au(1,4,5\text{-trimethyl-}1,2,4\text{-triazolium-}3\text{-thiolate})_2]BF_4$  (AuTT), which can be prepared by a substitution reaction between  $[Au(\text{tetramethylthiourea})_2]BF_4$  and the mesoionic thiolate. This complex, which has been structurally characterized by single-crystal X-ray diffraction, has good solubility and stability in water, both important properties for application in a robust commercial process. Recently a second generation Au(1+) chemical sensitizer has been introduced, potassium bis(1-[3-(2-sulfonatobenzamido)phenyl]-5-mercaptotetrazole potassium salt)aurate(I) (AuSBMT), an  $[Au(SR)_2]^{1-}$  type complex, which has significantly higher water solubility and somewhat better stability compared to AuTT. Another recently reported class of useful chemical sensitizers are dimeric Au(1+) complexes with 1,1-dithio ligands [e.g.,  $[AuS_2X]_2$ , X = COR (xanthates),  $CNR_2$  (dialkyldithiocarbamates),  $P(OR)_2$  (dithiophosphates),  $PR_2$  (dithiophosphinates)]. The thermal stabilities of the xanthate and dithiophosphate complexes are poor, but the dithiocarbamates and dithiophosphinates, exhibit good stability. The

dithiophosphinate complex,  $[\text{Au}(\mu\text{-S}_2\text{P}(\text{i-C}_4\text{H}_9)_2)_2]_2$ , which has excellent thermal stability and good solubility in methanol, has been structurally characterized by single-crystal X-ray diffraction (it has an intramolecular Au...Au bond distance of 3.17 Å, but, unlike many Au(1+) complexes of this general structural type, no intermolecular Au...Au interaction (i.e., the distance between gold atoms in neighboring dimers is 8.024 Å). These neutral complexes are insoluble in water, but stable aqueous dispersions, prepared by milling with a surfactant solution, can be used in emulsion sensitizations.

Although such chemical sensitizers are critical for the manufacture of modern high-speed photographic emulsions, the chemical identity of the sensitization centers that they form on silver halide grains during this process are not well characterized. Such sensitization centers form on the silver halide grain surface in a so-called “finishing step”, after the precipitation of the silver halides in aqueous gelatin. In this process, solutions of the gold and sulfur sensitizers are added to the emulsion, and the emulsion is heated to some fixed temperature, typically 50-75°C, where it is held to produce the desired sensitization, before being cooled to a lower temperature and coated on a paper or film base, typically polyethylene terephthalate (Estar base) for 35 mm film or, for the 24 mm film format of the Advanced Photo System (APS), polyethylene naphthalate (PEN). Unlike the situation with the other major class of inorganic reagents used in silver halide technology (dopants – generally anionic octahedral complexes of noble metals (e.g.,  $\text{K}_3[\text{IrCl}_6]$ ), which are added during the AgX precipitation process and incorporate intact in the silver halide lattice at very low levels and can be characterized by epr spectroscopy), the analytical difficulty of characterizing surface sensitization centers, complex chemical decomposition products involving the gold and sulfur compounds, and the silver halide, has proven to be a major challenge in silver halide emulsion technology. It is interesting to note that, although trace amounts of gold compounds are critical in silver halide technology to provide high speed commercial imaging elements, trace level gold contamination in silicon wafers used to fabricate CCD sensors for digital cameras results in significant dark current in such devices. Considerable effort is made to remove such low-level contamination by appropriate gettering processes, which concentrate the gold near the bottom of the wafer, removed from the active surface layer of the sensor.

Recently, the well-established luminescence of Au(1+) complexes has led to an interest in these materials as dopants in organic light emitting diodes (OLEDs), a new flat panel display technology invented at the Kodak Research Laboratories. Many such complexes exhibit phosphorescence, with emissions throughout the visible spectral region, lifetimes in the  $\mu\text{second}$  time regime, and emission quantum efficiencies of 0.1–0.3. Some typical Au(1+) compounds evaluated as OLED dopants will be described.