New Transition Metal Dopants with FED Ligands: Incorporating Two-Electron Sensitization Technology within the AgX Matrix

Thomas Pawlik, Jeffrey Hansen, Annabel Muenter, Donald Diehl, W. Gordon McDugle, Jerome Lenhard, and Raymond Eachus;
Research & Development, Eastman Kodak Company, Rochester, NY/USA

Abstract

Fragmentable two-electron donor compounds (FEDs) are molecules that have been designed to trap photoholes to create an unstable radical that, upon fragmentation, produces a second radical that is sufficiently energetic to inject a second electron into the silver halide conduction band. When added to the surface of a dispersion, these compounds significantly increase the light sensitivity of silver halide (AgX) materials. One potential improvement for these materials is a method to incorporate them into the interior of the silver halide matrix. Once incorporated, FEDs would not be able to redistribute in a dispersion mixture and might be protected from dark decomposition reactions that can lead to unwanted fog. We report our success in obtaining FED ligands that form transition metal complexes and in incorporating these new dopants into AgX dispersions. Photographic data showing the expected two-electron sensitization and electron paramagnetic resonance (EPR) data indicating dopant incorporation will be discussed.

Introduction

A method to substantially increase the imaging efficiency of state-of-the-art photographic materials has been reported by Gould et al. [1] and described in several patents [2-4]. This approach is summarized in Scheme 1.

Scheme 1

$$AgBr|Dye + h\nu \rightarrow AgBr|Dye^* \rightarrow (AgBr + e^-)|Dye^{\bullet+} \quad (1)$$

$$Dye^{\bullet+} + XY \rightarrow Dye + XY^{\bullet+} \quad (2)$$

$$XY^{\bullet+} \rightarrow X^{\bullet} + Y^+ \quad (3)$$

$$(AgBr + e^-) + X^{\bullet} \rightarrow (AgBr + 2e^-) + X^+ \quad (4)$$
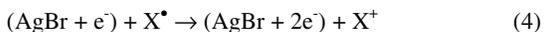
The photographic system, described as AgBr|Dye in Eq. 1, consists of silver halide microcrystals (or grains) dispersed in gelatin. These grains are usually spectrally sensitized with an adsorbed dye. The novel aspect of this scheme entails the co-addition of an electron donor molecule, XY. Light absorption by the dye initiates the transfer of an electron to the conduction band of the silver halide substrate [5], a condition represented here as $(AgBr + e^-)$. This is the first step in latent image formation [5]. The resultant oxidized dye radical, $Dye^{\bullet+}$, reacts with XY to give a radical cation, $XY^{\bullet+}$, which fragments to a radical $X^{\bullet}$ and a stable cation Y^+. XY is described as a fragmentable electron donor, or FED. Its structure is designed so that $X^{\bullet}$ is a powerful reductant and has the potential to transfer a second electron into the silver halide conduction band. Thus, two electrons are injected per absorbed photon, effectively doubling the imaging efficiency of

the system. This type of FED is referred to as a two-electron sensitizer, or TES. For energetic reasons, i.e., most efficient hole transfer from the dye to the FED, the FED process is most effective for blue- and green-sensitized dispersions.

One variation of the FED concept is to incorporate the FED into the silver halide grain. One obvious benefit is that the reactive FED moiety is shielded from environmental effects. We have pursued this approach by attaching an organic molecule with suitable properties as a ligand to an octahedral transition metal (TM) complex as a dopant. Previous experiments [6] have shown that the silver halide lattice is able to accommodate complex dopants with large organic ligands (OL). The octahedral transition metal complex serves as an "anchor", and close to 100% incorporation can be reached by this method. The incorporation of the dopant and charge neutrality is achieved by a suitable number of cation and anion vacancies. Examples for this class of dopants are Iridium-organic-ligand complexes used as electron traps to improve reciprocity law failure. By using a different OL, the electron trap lifetime can be adjusted for optimum effect on the reciprocity.

For the FED dopant complex, the TM-anchor moiety must be chosen so that is does not act as a deep electron trap. We have chosen the Osmium pseudohalide complex $Os(CN)_6$ as the basis for most of our work. This dopant can be a hole trap or shallow electron trap, depending on the degree of charge compensation [7,8].

Experimental Strategy

In order to function as a two-electron sensitizer in the silver halide system, three requirements are necessary for a FED dopant: the oxidation potential of the parent molecule must be low enough to allow the molecule to capture the photo-hole created in the silver halide; the fragmentation reaction must occur within the time scale of silver halide latent image formation; and the radical created by the fragmentation must be sufficiently reducing to inject an electron into the silver halide conduction band. The XY FED molecules selected for this study were amino acids, which, upon

Scheme 2
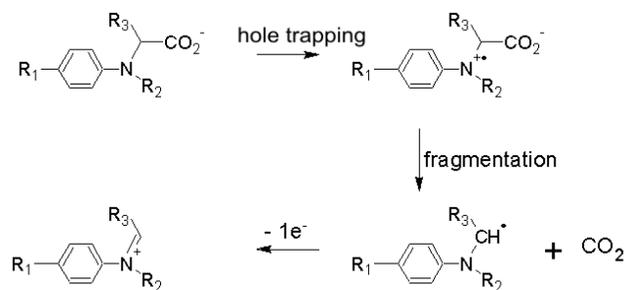
oxidation by a photo hole, are expected to give intermediates that can rapidly fragment by decarboxylation to α-amino radicals with strongly negative oxidation potentials [1]. In the amino acid structure shown in Scheme 2 above, the oxidation potential of the parent compound can be varied by changing the substituents R_1 and R_2. The fragmentation rate after oxidation is also strongly correlated with this oxidation potential, with compounds having lower oxidation potentials exhibiting slower fragmentation rates. The substituent R_3 influences the reducing power of the radical remaining after fragmentation. Radicals where R_3 is methyl have been found to have oxidation potentials more negative than –0.9 V, the condition required for the radical to easily inject an electron into the AgBr conduction band.

The organic ligands used in this study are shown in Table 1. The FED ligands are covalently bound to the TM complex through the N atom of a heterocycle. The "active" moiety (AM) that is designed to fragment after hole capture with CO_2 as the leaving group, is separated by a phenyl ring from the binding site. We have found that this separation is helpful in minimizing perturbation of the ligand oxidation potential by the complexed metal. TES-LG4 and –LG6 have the same AM but differ in the heterocycle that bonds to the TM. TES-LG5 and –LG6 differ in the structure of the AM. The methyl substituent in TES-LG6 makes this complex a more active species. Finally, OES is a molecule that can trap holes but cannot fragment. These ligands were attached to the TM complexes $Os(CN)_5$ and $Ir(Cl)_5$. Electron Paramagnetic Resonance (EPR) spectroscopy is an appropriate technique to test the FED dopant concept. It is able to detect photogenerated electrons and holes in the AgX matrix. It can also probe whether a dopant acts as a trap for holes or electrons. In particular, the introduction of a deep electron trap state is evidenced by the disappearance of the intrinsic EPR signal due to shallowly trapped electrons. This condition would be unfavorable
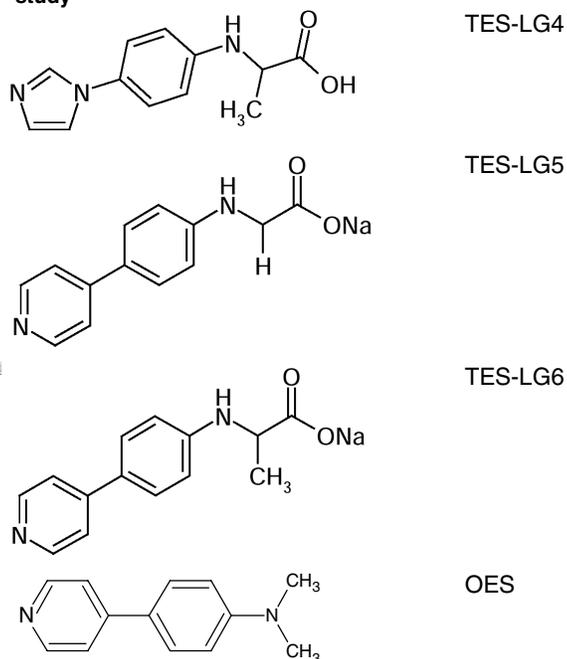
for a FED dopant. In order to stabilize the species generated upon photoexcitation, both exposure and EPR measurements were carried out at low temperatures. Changes in the EPR spectrum upon annealing of the sample provide information about the reactions among the photogenerated species. Doped silver halide dispersions for the EPR experiments were generated by a double jet precipitation technique with grain sizes of typically 0.1 μm.

Experimental Results

Figure 1 shows the X-band (9.30 GHz) EPR spectra of AgCl dispersions doped with 200 mppm of $Os(CN)_5$-TES-LG4 and –LG6 that were exposed to bandgap (365 nm) irradiation at 15 K. Some of the features in the EPR spectrum have been identified earlier. These are the $[AgCl_6]^{4-}$ self-trapped hole [9], the EPR signal due to shallowly-trapped electrons at a magnetic field value B = 354 mT (corresponding to a g-value of g = 1.88) [10], and features at B = 335 mT and 375 mT that are due to $[Os(CN)_5NO]^{3-}$ [11]. This latter species is due to a dopant impurity. $Os(CN)_5NO$ was used as the starting material for the Os-TES synthesis. An additional species is seen at B = 330 mT. The EPR spectrum of this feature in the –LG6 sample shows signs of g-matrix anisotropy. This is expressed as a deviation of the lineshape from a Gaussian envelope towards a powder pattern. We determined the g-matrix parameters (g_x, g_y, g_z) to be (2.021, 2.002, 2.002) for $Os(CN)_5$-TES-LG4, (2.034, 2.007, 1.994) for $Os(CN)_5$-TES-LG5, and (2.035, 2.008, 1.996) for $Os(CN)_5$-TES-LG6. The average g-value is higher than the g-value of the free electron (g = 2.0023), which is indicative of a trapped hole species on an organic molecule. The fairly large positive g-shift suggests that there is some degree of admixture of metal wavefunctions to the ground state of the hole trap species. Due to the large spin-orbit coupling of Os, only a small unpaired electron density on the metal is needed to influence the g-values. This in turn shows that the molecular structure of the dopant is intact in the doped dispersions. In Os-TES-doped AgBr dispersions, similar EPR spectra are observed upon bandgap irradiation. We find that, after bandgap (440 nm) exposure at 15 K,

Table 1: Molecular structure of the organic ligands used in this study

TES-LG4

TES-LG5

TES-LG6

OES
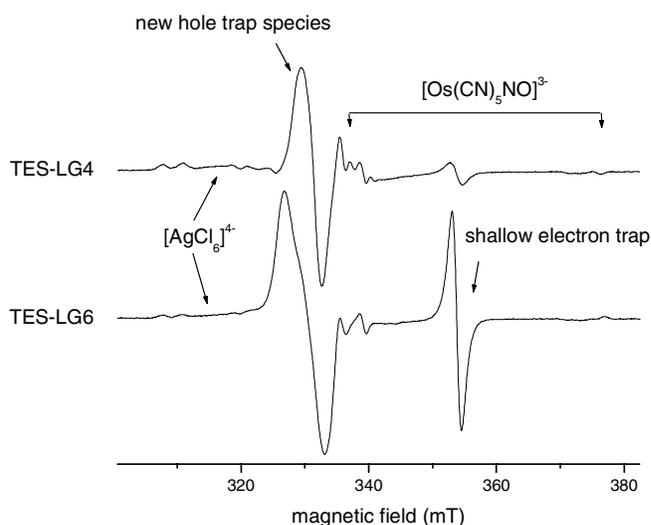
Figure 1. EPR spectra of AgCl dispersions doped with 200 mppm of $Os(CN)_5$-TES-LG4 and –LG6, exposed to 365 nm irradiation at 15 K

the EPR intensity of the surface-related intrinsic hole center $[Br_4.V_{Ag}]^{3-}$ [9] is much lower in a $Os(CN)_5$-TES-LG4 doped emulsion compared to an undoped check. In addition, the dopant-related EPR signal appears along with the EPR signal from shallowly trapped electrons at irradiation wavelengths greater than 540 nm, i.e., below the bandgap of AgBr. This suggests a dopant-to-conduction band excitation that creates trapped holes on the dopant and shallowly trapped electrons. Both observations are consistent with the dopant acting as a hole trap. The g-matrix parameters of the Os-TES dopants in AgBr are very similar to the values observed in AgCl, however, slight differences can be resolved by measuring EPR spectra in Q-band (35 GHz).

One challenge for the investigation of the FED-dopant concept is to prove that the dopant is indeed incorporated into the silver halide matrix and not carried to the surface of the grain. Several studies were undertaken to deliver evidence for this hypothesis. Figure 2 shows EPR spectra of three AgBr dispersions after bandgap exposure at 15 K: a) AgBr doped with $Os(CN)_5$TES-LG6 (200 mppm); b) AgBr sensitized with $Os(CN)_5$TES-LG6 (1000 µmol/mol AgBr); c) AgBr sensitized with TES-LG6 (3000 µmol/mol AgBr). The signal in a) attributed to the hole trap state of the $Os(CN)_5$TES-LG6 dopant does not appear in the other two samples. Trace c) shows a strong EPR signal indicative of the hole trap state of the TES-LG6 ligand. This species has a g-value of 2.003, close to the value of the free electron. Similar signals were observed previously in AgBr dispersions sensitized with FED molecules [12]. They could be assigned to the hole trap species of the FED molecule. Trace b), which is the dispersion sensitized with $Os(CN)_5$TES-LG6, shows some signature of the signal in c) and also broader signal that is shifted to lower g-values. The appearance of these two signals could be due to a fragmentation of the $Os(CN)_5$TES-LG6 moiety leading to a hole trap signal of free TES-LG6 and another Os-related species. We did not attempt to identify the latter species, however, we conclude that the EPR signal in a) is unique to the dispersion doped with $Os(CN)_5$TES-LG6 and does not appear

a)

b)

c)
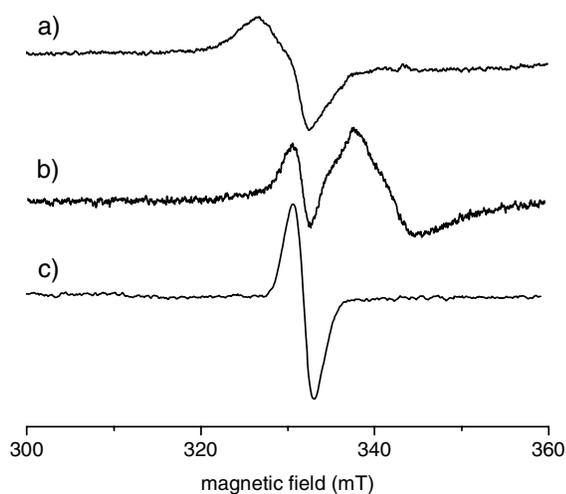
Figure 2. EPR spectra of three AgBr dispersions after bandgap exposure (440 nm) at 15 K: a) AgBr doped with $Os(CN)_5$TES-LG6 (200 mppm); b) AgBr sensitized with $Os(CN)_5$TES-LG6 (1000 µmol/mol AgBr); c) AgBr sensitized with TES-LG6 (3000 µmol/mol AgBr)

when the dopant is added after precipitation as a sensitizer.

Further proof of dopant incorporation can be obtained by studying the lattice surroundings of the dopant. Electron-Nuclear Double Resonance (ENDOR) is a sensitive technique to resolve small hyperfine interactions of the unpaired electron of the FED
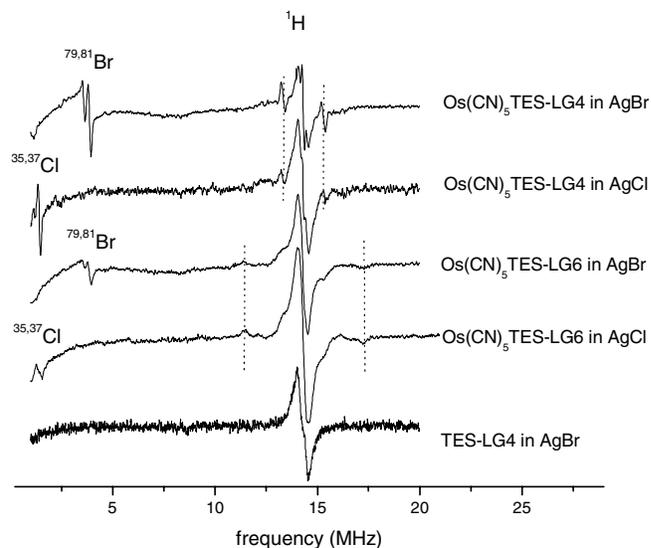
Figure 3. ENDOR spectra of four silver halide dispersions doped with $Os(CN)_5$-TES-LG4 and –LG6 and one AgBr dispersion doped with the organic ligand only.

species with its surrounding nuclei. These nuclei can be protons of the organic molecule itself or lattice nuclei of the silver halide matrix. In the latter case, the hyperfine interaction is often so small that only a single line at the Larmor frequency of the isotopes ^{107,109}Ag, ^{35,37}Cl, or ^{79,81}Br, is observed. Figure 3 shows ENDOR spectra of AgCl and AgBr doped with $Os(CN)_5$TES-LG4 and –LG6. In addition, an ENDOR spectrum from a AgBr dispersion doped with the ligand TES-LG4 is shown. The spectra were obtained by saturating the EPR spectrum of the hole trap state of the dopant. The features indicated by dotted lines, spaced symmetrically about 14 MHz, the Larmor frequency of ^{1}H, are due to protons of the TES molecule. Similar signals were observed for other TM-organic ligand dopants [13]. Note that the line positions are similar for the same dopant in the two matrices (AgBr and AgCl). In addition to these features, we observe ENDOR signals from ^{35,37}Cl and ^{79,81}Br for the doped AgCl and AgBr dispersions, respectively, but not for the AgBr dispersion that was doped with the TES-LG4 ligand. It is reasonable to conclude that the EPR signal in the latter sample is due to hole trapped species on the surface of the AgBr grain. This is another argument in favor of the octahedral TM complex mediating dopant incorporation in the silver halide matrix. Elemental analysis of the doped dispersions shows an incorporation of Os of about 30%. From our experience, the incorporation of TM-OL complexes based on $IrCl_6$ is better and can reach 100%. $IrCl_5$-OL species in silver halides can act as electron traps. However, the electron trap lifetime is dependent on the OL and can be optimized to not impede the photographic efficiency of the silver halide dispersion [14]. Thus, in an initial attempt to prepare Ir-based FED dopants, we generated the

complex IrCl$_5$-OES (see Table 1), in which the ligand is designed to be able to trap photogenerated holes but does not fragment.
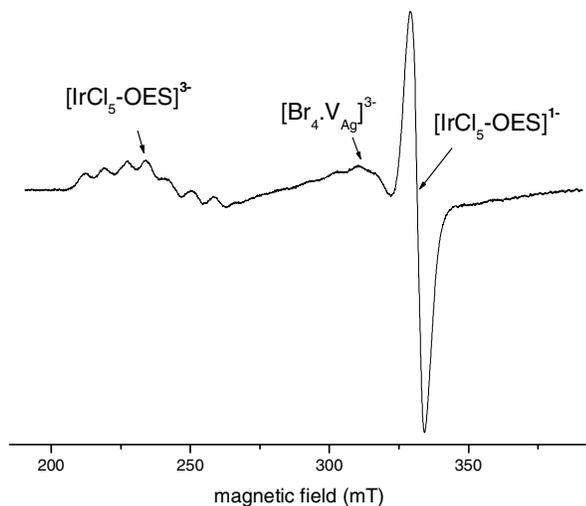
Figure 4. EPR spectrum of a AgBr dispersion doped with IrCl5-OES and irradiated with bandgap light (440 nm) at 15 K

Figure 5. Plot of optical density vs log Exposure of coatings of four blue-sensitized photographic emulsions with dopant concentrations as indicated.

Figure 4 shows the EPR spectrum of a AgBr dispersion doped with IrCl$_5$-OES after bandgap irradiation at 15 K. The EPR signal at 230 mT is due to a trapped electron species on the Ir atom. The g-matrix parameters of (2.98, 2.67, 1.82) are similar to other Ir-OL trapped electron species [6]. The broad derivative signal with a zero transition at 320 mT is due to an intrinsic hole center [Br$_4$.V$_{Ag}$]$^{3-}$ close to the grain surface [12]. An additional EPR signal at 332 mT is also found in a similarly prepared dispersion when Os(CN)$_5$-OES is used as a dopant. It is reasonable to assign this signal to the hole trap state of the dopant. Thus, for the IrCl$_5$-OES dopant, we have a situation where the dopant can act both as an electron trap and as a hole trap. In the former case, the unpaired electron is situated in a 5 d orbital on the Ir atom. In the latter case the unpaired electron is situated on the OES ligand.

As an example of the effect of the Os(CN)$_5$-TES-LG5 dopant on the sensitivity of a AgBrI dispersion, we show in Figure 5 the optical density of coatings of four blue-sensitized photographic dispersions. The feature dispersions consisted of an undoped AgBrI host with a doped 2.5% AgBr shell at two nominal levels of the dopant. Also plotted is the dispersion without a dopant and without a shell as comparisons. We clearly observe a gain in efficiency (>0.1 logE) from the dopant. At the lower dopant level, the minimum optical density (fog) and granularity (not shown) are not elevated with respect to the undoped core-shell dispersion. Only at the higher dopant level of 2.5 mppm is there a penalty both in minimum density and granularity from the addition of the dopant.

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Author Biography

Thomas Pawlik is a Senior Research Scientist in the Foundation Science Center within Research & Development at Eastman Kodak Company. He received his PhD in solid-state physics from the University of Paderborn, Germany. His research interests include the photophysics of oxide semiconductors and silver halide imaging materials and charge transport and recombination in organic semiconductors.