

# Structure of the Trimer Silver Cluster $\text{Ag}_3^{2+\dagger}$

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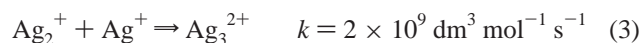
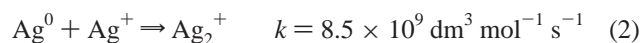
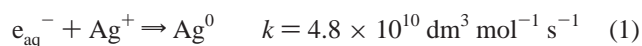
During the growth of small colloidal silver clusters in aqueous solution, the trimer silver ion exhibits a remarkable behavior in that this species represents the changeover from pseudo-first-order reaction mechanisms to second-order mechanisms. The model for the molecular structure of the trimer silver ion which is proposed here on the basis of divalent silver explains this observation and the formation of “magic” clusters.

## Introduction

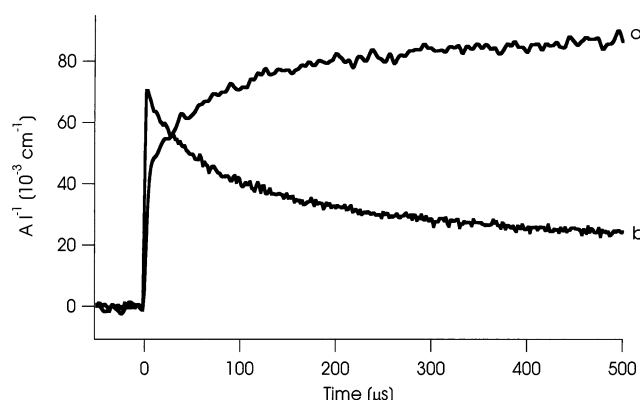
Recently, trimer silver clusters have been identified during the growth of silver clusters initiated by the reduction of silver ions in aqueous solution.<sup>1</sup> In these experiments, the irradiation dose was so low that only a small amount of bulk silver ions was reduced. The reduced silver ion reacts in a two-step mechanism with two bulk silver ions, yielding first the dimer cluster and then the trimer cluster. Each step of the formation of the trimer silver cluster was found experimentally to follow strictly a pseudo-first-order law with regard to silver ion concentration. On the other hand, the subsequent reaction, i.e., the disappearance of the trimer silver cluster, follows a second-order law despite the presence of a large amount of bulk silver ions in solution. Further reactions also seem to be second-order reactions. Whereas the formation of the trimer cluster occurs within a few microseconds, at low concentration its disappearance takes place within a few milliseconds, demonstrating the relative stability of this species. Therefore, the question arises—what is special about trimer silver clusters—because they represent a transition point in the reaction mechanism describing the growth of small silver clusters. A model of the molecular structure of the trimer silver cluster is proposed here in order to answer this question and, at the same time, to offer an explanation for the formation of “magic” clusters.

## Experimental Results

When an aqueous solution containing silver ions is irradiated using high energy electrons, the resultant hydrated electrons quickly reduce bulk silver ions which subsequently react with remaining bulk silver ions<sup>1</sup> according to

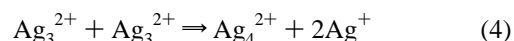


The free silver atom has a characteristic absorption band at 360 nm, while the dimer silver cluster absorbs at 310 nm. The trimer silver cluster has two absorption bands, one at 265 nm and one at 310 nm. The product of the second-order disappear-



**Figure 1.** Optical absorption curves at 260 (a) and 310 nm (b) observed in an aqueous solution of  $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ AgClO}_4$ ,  $0.3 \text{ mol dm}^{-3} \text{ 2-PrOH}$  at natural pH, and purged with Ar. Irradiation dose corresponds to  $5 \times 10^{-6} \text{ mol dm}^{-3} \text{ e}_{\text{aq}}^-$ ; the absorbivity ( $A$ ) is normalized to the cell length ( $l$ ).

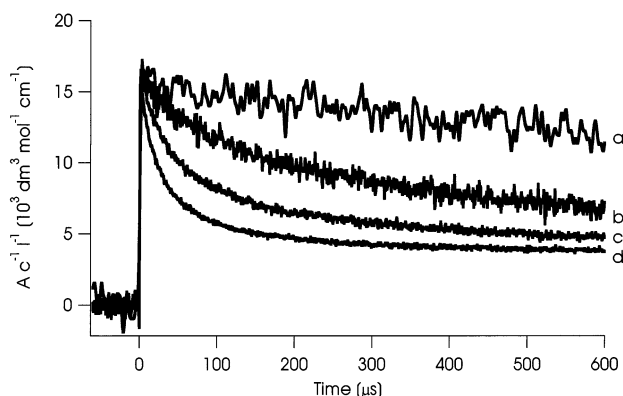
ance of the 310 nm species carries two elementary charges, as was concluded from the kinetic salt effect on their bimolecular disappearance.<sup>2</sup> The species  $\text{Ag}_4^{2+}$  is therefore attributed to the product of the bimolecular disappearance of the trimer cluster according to



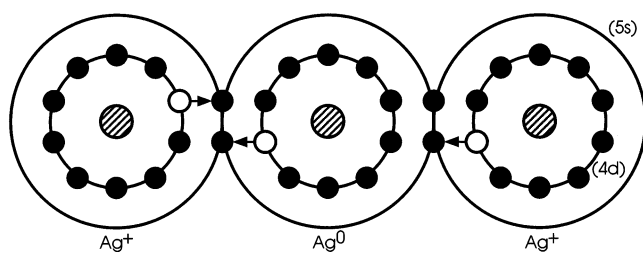
The tetramer cluster exhibits an absorption band at 265 nm. Due to the overlapping absorption bands with the dimer on one hand and the tetramer on the other, the trimer silver cluster was overlooked for a long time. Figure 1 shows the changes in absorption at 260 and 310 nm following the pulse radiolytic reduction of a small amount of silver ions. The absorption at 310 nm exhibits an instantaneous buildup and subsequent decay, whereas at 260 nm there is an initial steep increase followed by a slow one. The steep increase at 260 nm is slower than the instantaneous buildup at 310 nm. The initial increase of the 310 nm absorption is caused by the formation of the dimer cluster, whereas the decay is due to the disappearance of the trimer cluster. The steep increase of the 260 nm absorption is due to the formation of the trimer cluster, while the slow increase is attributed to the formation of the tetramer cluster. The rate of the slow increase at 260 nm corresponds to the rate of the decay at 310 nm. The formation of the tetramer cluster is purely a second-order reaction. This is demonstrated in Figure 2, where

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**Figure 2.** Decay of absorption at 310 nm for various irradiation doses. Solution as in Figure 1. Dose corresponds to (a)  $3 \times 10^{-7}$ , (b)  $2 \times 10^{-6}$ , (c)  $7 \times 10^{-6}$ , and, (d)  $1.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ e}_{\text{aq}}^-$ ; the absorptivity ( $A$ ) is normalized to the cell length ( $l$ ) and to the radical concentration ( $c$ ).

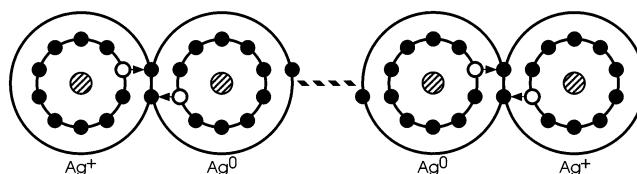


**Figure 3.** Hypothetical model of the structure of the trimer silver cluster  $\text{Ag}_3^{2+}$ .

the decay of the trimer cluster is shown for various irradiation doses. Computer simulation<sup>3</sup> of these decay curves yields a second-order rate constant of  $2k_4 = 2.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . It should also be noted that no change in conductance was measured during the growth of silver clusters.<sup>4</sup>

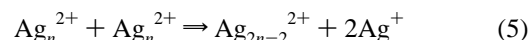
### Structure of $\text{Ag}_3^{2+}$

The trimer cluster can be seen to be a fairly stable intermediate. This is certainly surprising because the charge is rather high for such a small cluster so that Coulombic repulsion could be expected. In general, it is difficult to imagine a model for the structure of the trimer cluster based on monovalent silver. On the other hand, stable molecules of divalent silver are known, such as  $\text{AgO}$ ,<sup>5,6</sup> or inorganic<sup>7</sup> and organic<sup>8</sup> complexes, or silver nanoclusters.<sup>9,10</sup> In general, the electronic configuration of silver is  $[\text{Kr}]4d^{10}5s^1$ . The  $5s^1$  shell is the principal valence orbital, which accounts for the preference for oxidation state 1. The  $4d$  shell can also act as a valence orbital, resulting in oxidation states 2 and 3. Thus, silver behaves as a transition metal due to the contribution from the inner valence orbital. Since the difference between the energies of the valence electrons is small, silver has a tendency to form complexes with covalent bonds.<sup>11,12</sup> With this in mind, one can imagine trimer clusters of divalent silver<sup>13</sup> with a valence electron configuration as shown in Figure 3. The free silver atom is in the center position between both—nonreduced—silver ions. From the free silver atom, two valence electrons are available for the bonds, one in the  $5s$  orbital and an additional one from the  $4d$  orbital. Both silver ions each contribute only one valence electron from the  $4d$  shell. In this case, exactly four valence electrons are available to form two electron pair bonds. Each silver atom behaves the same way by involving one electron from the  $4d$  shell in the bonds. If oxidation state 2 is assumed to persist, no further silver ion can dock onto the cluster. On the other hand, recombination reactions



**Figure 4.** Hypothetical model of the growth of larger silver clusters.

are possible by splitting off one silver ion from each reactant, thus forming the tetramer cluster as described by reaction 4. The recombination process, if it continues according to the same pattern, would lead to the “magic” clusters  $\text{Ag}_6^{2+}$ ,  $\text{Ag}_{10}^{2+}$ ,  $\text{Ag}_{18}^{2+}$ ,  $\text{Ag}_{34}^{2+}$ , etc., or, in general



by which small linear clusters of  $m$  silver atoms are formed as a chain consisting of  $m - 2$  free silver atoms and two nonreduced silver ions, one at either end of the chain, i.e.,  $\text{Ag}^+(\text{Ag}^0)_{m-2}\text{Ag}^+$ . Such a model is shown in Figure 4. The structure of the silver cluster will change with increasing growth from the linear configuration, perhaps via coiling, to a crystalline one. Because the specific conductance of the bulk silver ion  $\text{Ag}^+$  and of the silver ions in the cluster would not significantly differ, the change in measured conductivity should be marginal during growth.

### Discussion

In the study of small metal clusters in aqueous solution, attention focuses on using silver clusters as a model. The monovalent cation  $\text{Ag}^+$  is the only noble cation that forms mononuclear species with appreciable stability in aqueous solution so that no hydrolysis occurs.<sup>14</sup> The existence of the trimer silver cluster  $\text{Ag}_3^{2+}$  was discovered in ESR studies on  $\gamma$ -irradiated frozen solutions of  $\text{AgClO}_4$  in toluene,<sup>15</sup> and later seen in numerous studies on zeolites containing silver ions.<sup>16–24</sup> More recently,  $\text{Ag}_3^{2+}$  clusters were also detected in glassy water–alcohol solutions,<sup>25</sup> as well as in aqueous solutions at room temperature,<sup>1</sup> where silver salts were present. Although attempts were made to reveal the structure of  $\text{Ag}_3^{2+}$  in different zeolites by interpreting various experiments and by taking theoretical considerations into account, nothing is known about the structure of this species in water at room temperature. The interpretation of various experiments involving silver in zeolites even led to contradictory models. From experimental data, the structure of the trisilver cluster  $\text{Ag}_3^{2+}$  in various zeolites was proposed to be either linear<sup>16–22</sup> or triangular.<sup>23,24</sup> Theoretical calculations support the linear structure<sup>26,27</sup> as well as the triangular structure.<sup>23</sup> Diamagnetic  $\text{Ag}_4^{2+}$  was observed in hydrated samples of  $\gamma$ -irradiated  $\text{AgCs}$ -rho zeolites at room temperature.<sup>28</sup> ESR and optical absorption measurements in glassy aqueous solutions or glassy aqueous–alcoholic solutions reveal a linear structure of the trisilver cluster.<sup>25</sup>  $X_\alpha$  scattered-wave calculations of the transition energies of a linear trimer silver cluster postulate absorption bands<sup>29</sup> which are in good agreement with the ones observed here at 265 and 310 nm. Dirac scattered-wave calculations for  $\text{Ag}_3^{2+}$  demonstrate that the lower lying occupied molecular orbitals also participate in the cluster bonding.<sup>30</sup>

There have been no time-resolved ESR measurements reported for the fairly long-lived trisilver cluster in aqueous solution, and no theoretical calculations on its structure as well. The approximation of the structure of larger clusters in aqueous solution depends intuitively on the growth mechanism being

proposed. Comparing the structure of  $\text{Ag}_3^{2+}$  obtained in the stabilizing cage of a zeolite to that of this species when surrounded by water molecules might also be questionable. The structure of larger silver clusters in water might follow a linear structure, as mentioned above, but could also be a closed one such as a tetrahedron for the silver tetramer and might lead to other "magic" clusters such as the  $\text{Ag}_{10}$  cluster possibly of a higher order tetrahedral structure intimately related to adamante.

## Conclusions

A simple hypothetical model of the trimer silver cluster  $\text{Ag}_3^{2+}$  is presented making use of divalent silver. This model can explain experimental observations such as the relative stability of trimer clusters and also the formation of silver clusters of a specific number of atoms, i.e., the "magic" clusters. The trimer silver clusters described above should exhibit diamagnetic properties; it would be desirable to verify this concept with ESR/EPR measurements.

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