A Novel Silver Cluster

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The pentameric silver cluster, $Ag_5{}^{4+}$, has been prepared in methanol and ethanol glasses at 77 K and characterised by e.s.r. and optical spectroscopies; the experimental parameters for this species are in close agreement with previous theoretical studies.

The study of silver aggregates is of great interest in the fields of surface physics and chemistry, heterogenous catalysis, and the photographic process.[1] The neutral species $Ag_3{}^0$ and $Ag_5{}^0$ have been prepared by vapour deposition into organic matrices at 77 K and characterised by e.s.r. spectroscopy.[2,3] In addition, the clusters $Ag_n{}^0$ ($n = 2$—7) have been characterised in inert gas matrices by optical techniques.[4] E.s.r. and optical data also exist for the cationic clusters $Ag_2{}^+$, $Ag_3{}^{2+}$, and $Ag_4{}^{3+}$, formed by γ-radiolysis of aqueous and organic glasses at 77 K.[5,6] A cluster described as $Ag_6{}^{n+}$ has been reported in Na–A and Na–Y zeolites.[7] We now report the e.s.r. and optical data for the pentameric unit $Ag_5{}^{4+}$. A binomial quartet e.s.r. spectrum tentatively assigned to this species has recently been reported for a zeolite matrix,[8] formed by the reaction of the $Ag_6{}^+\cdot 8Ag^+$ cluster with ethene. This result, which differs from ours, is discussed below.

The e.s.r. spectrum of a 0.05 M solution of silver perchlorate in methanol after exposure to ^{60}Co γ-rays at 77 K revealed features attributable to silver atoms, together with weak features due to $Ag_2{}^+$. On annealing this sytem, the higher nuclearity clusters $Ag_3{}^{2+}$ and $Ag_4{}^{3+}$, formed according to reactions (1), were detected.[6]

$$Ag^0 \xrightarrow{Ag^+} Ag_2{}^+ \xrightarrow{Ag^+} Ag_3{}^{2+} \xrightarrow{Ag^+} Ag_4{}^{3+} \qquad (1)$$

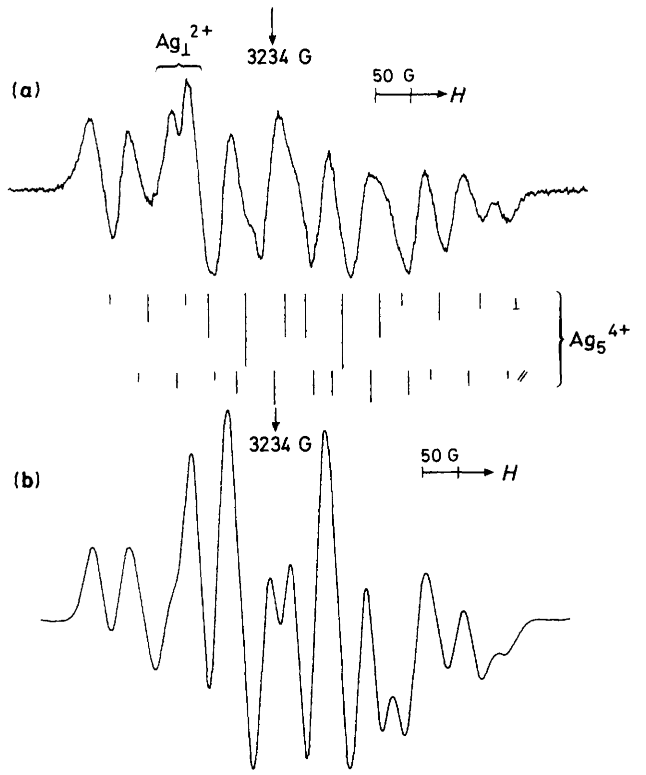

Figure 1. (a): First derivative *X*-band e.s.r. spectrum for 0.5 M $AgClO_4$ in methanol after exposure to ^{60}Co γ-rays at 77 K and annealing to *ca.* 120 K, showing features assigned to Ag_5^{4+} ions, and associated stick diagram. Features for residual Ag_4^{3+} ions are largely beneath the main spectrum. The positions for the two perpendicular features for Ag^{2+} ions are indicated, the parallel features being at low field, outside the range of the spectrum. (b): Simulated *X*-band e.s.r. spectrum for Ag_5^{4+} using $g_{\parallel} = 1.946$, $g_{\perp} = 1.979$, A_{iso} Ag(3) = (−)140 G, A_{iso} Ag(1) = (−)64 G and A_{iso} Ag(1) = (−)46 G, and a linewidth of 16 G. As discussed in the text, the experimental spectrum is modified by the presence of underlying signals from Ag_4^{3+}, Ag^{2+} and Ag^+CH_2OH (1 G = 10^{-4} T).

Using more concentrated solutions (*ca.* 0.5 M $AgClO_4$) a new set of features appeared on annealing to *ca.* 120 K. The e.s.r. spectrum (Figure 1) is interpreted as a quartet of triplets, arising from a set of three and a set of two nearly equivalent silver atoms. This spectrum is assigned to an Ag_5^{4+} centre, having a trigonal bipyramidal structure. The hyperfine parameters are discussed in detail below. On further annealing, residual features for Ag_4^{3+} were detected at temperatures as high as 160 K, whereas the pentamer decayed at *ca.* 130 K. This behaviour supports Baetzold's predictions of higher stability for silver particles having an even number of atoms, compared to those having an odd nuclearity.[9]

Ozin *et al.*[10] have predicted hyperfine interactions for a ligand-free trigonal bipyramidal Ag_5^{4+} centre of −121 G (3 equatorial atoms) and −71 G (2 axial atoms). These parameters are in good agreement with the experimental data, allowing for matrix interactions and the possible presence of surrounding ligands. The predicted *g*-tensor components are greater than those found experimentally, but the estimate of $g_{\parallel} < g_{\perp}$ is in agreement with experiment; $g_{\parallel}$ (exp.) = 1.946 [$g_{\parallel}$ (calc.) = 2.0467] and $g_{\perp}$ (exp.) = 1.979 [$g_{\perp}$ (calc.) = 2.1497]. Figure 2 shows a simulated e.s.r. spectrum for Ag_5^{4+}, incorporating an axial *g*-tensor. It was found that the best fit to the experimental data was obtained using somewhat inequivalent axial silver hyperfine splittings of −46 and −64 G, with the three equatorial atoms giving rise to a hyperfine coupling of −140 G each. The spectrum is modified to a certain extent by the presence of underlying features for Ag^{2+}, Ag_4^{3+}, and Ag^+CH_2OH.

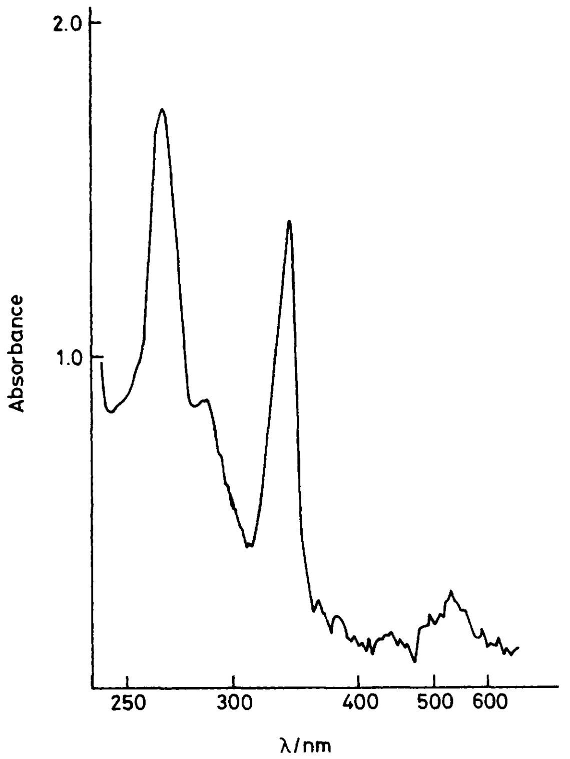

Figure 2. Optical spectrum of a 0.50 M $AgClO_4$ in ethanol solution after exposure to ^{60}Co γ-rays at 77 K and annealing to *ca.* 120 K.

The optical spectrum shown in Figure 3 was obtained using a sample whose e.s.r. spectrum revealed the presence of Ag_4^{3+} and Ag_5^{4+}. In addition to the band at 265 nm associated with the tetramer,[6] three new bands are present at 286 nm, 333 nm and 525 nm. These are in reasonable agreement with the theoretical values.[10] The band at 525 nm is responsible for the pink colour of these samples.

We consider that the agreement between our data and theoretical predictions provide strong support for an assignment to Ag_5^{4+}. If this is correct, it seems that the quartet reported previously[8] is not due to Ag_5^{4+}. Probably the ethene is incorporated into this unit.

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References

1 See, for example: M. D. Morse, *Chem. Rev.*, 1986, **86**, 1049.
2 J. A. Howard, K. F. Preston, and B. Mile, *J. Am. Chem. Soc.*, 1981, **103**, 6226.
3 J. A. Howard, R. Sutcliffe, and B. Mile, *J. Phys. Chem.*, 1983, **87**, 2268.
4 G. A. Ozin and H. Huber, *Inorg. Chem.*, 1978, **17**, 155.
5 C. E. Forbes and M. C. R. Symons, *Mol. Phys.*, 1974, **27**, 467.
6 A. D. Stevens and M. C. R. Symons, *Chem. Phys. Lett.*, 1984, **109**, 514; A. D. Stevens, Ph.D. Thesis, Leicester University, 1985.
7 D. Hemerschmidt and R. Haul, *Ber. Bunsenges Phys. Chem.*, 1980, **84**, 902.
8 J. R. Morton, K. F. Preston, A. Sayari, and J. S. Tse, *J. Phys. Chem.*, 1987, **91**, 2117.
9 R. C. Baetzold, *Phot. Sci. & Eng.*, 1973, **17**, 1978.
10 G. A. Ozin, S. A. Mattar and D. F. McIntosh, *J. Am. Chem. Soc.*, 1984, **106**, 7765.