Silver(I) Imidazole Perchlorate. An $(Ag^+)_6$ Cluster and its Radiolytically Produced One-electron Adduct studied by *X*-Ray Diffraction and Electron Spin Resonance Spectroscopy †

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The crystal structure of silver(I) imidazole perchlorate reveals the presence of a planar $(Ag^+)_6$ cluster, in which three radiating pairs of Ag^+ ions 3.051(1) Å apart are disposed on the corners of an equiliateral triangle, the inner Ag^+ ions being 3.493(1) Å apart. Each silver ion carries two linearly co-ordinated imidazole ligands, the whole unit has 32 (D_3) symmetry. Exposure to ^{60}Co γ-rays at 77 K results in electron addition to a group of three equivalent silver atoms. The ^{109}Ag, ^{107}Ag, and ^{14}N hyperfine coupling constants show that the total 5*s* character of the unpaired electron is only *ca.* 0.55, and delocalisation onto six equivalent nitrogen ligands accounts for *ca.* 0.25. Low *g* values suggest that the remaining spin density is in 5*p* orbitals on silver. There is no indication of delocalisation onto the remaining three Ag^+ ions in the cluster. Possible reasons for this selectivity are discussed. The electron-loss centre appears to be a normal Ag^{2+} complex. We suggest that marked distortion results in the hole being trapped on one silver rather than being delocalised.

SILVER exhibits a remarkable tendency to form clusters. In the presence of a single electron in excess, reaction to give Ag_2^+ and Ag_4^{3+} units is extremely facile even at low temperatures.[1,2] This property probably contributes to the efficacy of silver halides in the primary photographic process. One curious facet of our studies of this aggregation process by e.s.r. spectroscopy is that when Ag^0 centres are formed in glasses dilute in Ag^+ ions, they form Ag_2^+ followed by Ag_4^{3+} centres on annealing, without any accumulation of Ag_3^{2+} centres. These centres were, however, detected in irradiated toluene glasses containing dissolved silver perchlorate.[3]

In studies of the effect of high-energy radiation on silver salts, there is a marked difference between nitrates and perchlorates. Silver nitrate crystals gave NO_3^{2-} rather than Ag^0 as the primary electron-gain centre,[4,5] with Ag^{II} as the major electron-loss centre. Solutions of silver nitrate in cyanomethane gave Ag^0 centres in addition to NO_3^{2-} and NO_2, but the e.s.r. spectra for the Ag^0 centres displayed no ^{14}N hyperfine coupling, and were thus not formed from simple solvated $Ag(NCMe)_4^+$ ions, but rather from ion clusters.[5] In contrast, solutions of silver perchlorate in cyanomethane gave high yields of $Ag^0(NCMe)_4$ showing hyperfine coupling to four equivalent ^{14}N nuclei.[6,7]

The imidazole ligands are linearly co-ordinated to Ag^I in bisimidazolesilver(I) nitrate.[8] We have shown[9] that the effect of ionizing radiation on single crystals of this material is to give Ag^{II}, whose e.s.r. spectrum shows the presence of two equivalent ^{14}N nuclei, together with NO_2 radicals. Again, there is no tendency for the Ag^I ions to add electrons. One aim of the present study was to generate $Ag^0(imid)_2$ (imid = imidazole) centres and the perchlorate salt was prepared in the expectation that this centre would be formed on exposure to ionizing radiation. This expectation was realised with one crystalline form, but the most stable crystalline form of the imidazole perchlorate gave a centre whose e.s.r. spectrum indicated electron attachment to three equivalent Ag^I ions. This result suggested that the crystal structure would be worth studying. In fact, well defined clusters involving six Ag^I ions have been detected.

Other examples of silver(I) clusters include an N-bridged dimeric complex with an Ag $\cdots$ Ag separation of 3.177 Å, suggesting a weak silver–silver 'bond'.[10] Also, Teo and Calabrese[11] prepared and studied some tetrameric triphenylphosphine silver(I) halide complexes having distorted tetrameric cubane structures with halide-ion bridges. A remarkable octahedral cluster, Ag_6, has been detected in dehydrated silver(I) exchanged zeolites.[12,13] In the complex, which was described as $(Ag^+)_6(Ag_6)$,[13] the Ag–Ag separation was 2.850 Å and the $Ag–Ag^+$ separation was 3.26 Å.

EXPERIMENTAL

Silver(I) imidazole perchlorate was prepared from aqueous silver perchlorate and aqueous imidazole. The resulting precipitate was treated with perchloric acid to give a white crystalline solid which was recrystallised from ethanol or acetone {Found: C, 20.85; H, 2.20; N, 16.5. Calc. for $[Ag_3(C_3N_2H_4)_6][ClO_4]_3$: C, 21.0; H, 2.35; N, 16.3%}. Infrared and ^1H n.m.r. spectra confirmed the purity of the compound.

Samples were irradiated as fine powders in a Vickrad ^{60}Co γ-ray source at 77 K for up to 2 h at a dose rate of *ca.* 2 Mrad h^{-1}. Electron spin resonance spectra were measured at 77 K or above on a Varian E3 spectrometer, calibrated with diphenylpicrylhydrazyl (dpph). Single crystals were grown from ethanolic solutions.

X-Ray Structure Determination.—Crystal data. $C_6H_8AgClN_4O_4$, $M = 343.5$, Rhombohedral, $a = 20.09(2)$ Å, $\alpha = 42.1(1)^\circ$ (hexagonal cell $a = 14.444(10)$, $c = 54.84(4)$ Å), $U = 3\,302.5$ Å^3, $D_m = 2.05$ g cm^{-3}, $Z = 12$, $D_c = 2.072$ g cm^{-3}, $F(000) = 2\,016$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å) μ(Mo-K_α) = 19 cm^{-1}. Space group $R\bar{3}c$ (see below).

Data collection, structure solution and refinement. Preliminary Weissenberg and precession photographs suggested

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† Taken as Part 191 of Unstable Intermediates. Part 190, D. R. Smith, M. C. R. Symons, and P. Wardman, *J. Phys. Chem.*, 1979, **83**, 1762.

a monoclinic unit cell with systematic absences consistent with space groups *C*2/*c* or *Cc*, and intensity data were collected on that basis. An automatic Stoe–Güttinger Weissenberg diffractometer equipped with graphite-monochromated Mo-K_α radiation was used to collect layers *h*(0—14)*l* from a well formed crystal, dimensions *ca.* 0.2 × 0.2 × 0.3 mm, mounted about the unique *b* axis. Cell dimensions determined by careful setting angle measurements were $a = 25.022$, $b = 14.436$, $c = 20.092$ Å, $\beta = 114.5°$. A variable *w*-scan technique[14] was employed, using parameters determined from strong reflections, and a reflection chosen from each layer was remeasured every 30 reflections to check the stability of crystal and instrument, which proved satisfactory. A total of 4 853 independent reflections having $7 \leqslant 2\theta \leqslant 60°$ and $I \geqslant 3\sigma(I)$ were obtained and corrected for Lorentz and polarisation, but not absorption ($\mu R = 0.2$) effects.

Four independent silver atoms, two in general positions and two in special positions with site symmetry 2 of space group *C*2/*c*, were located by Patterson summation, and the remaining non-hydrogen atom positions were found from a difference-Fourier synthesis. Block-diagonal least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms, and hydrogen atoms in calculated positions, converged with $R = 0.031$. [$R' = 0.025$ with $w = 1.0/(2.3 - 0.17F + 0.004F^2)$.] Nitrogen atoms were assigned from chemical, temperature-factor, and bond-length considerations.

TABLE 1

Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
As(1)	0.139 61(3)	0.139 61(3)	0.250 00
As(2)	0.350 84(3)	0.350 84(3)	0.250 00
Cl(1)	0.535 53(8)	0.448 39(7)	0.200 64(1)
O(1)	0.444 3(3)	0.342 0(3)	0.201 56(6)
O(2)	0.546 6(3)	0.498 5(3)	0.223 87(5)
O(3)	0.522 0(4)	0.508 9(3)	0.181 91(6)
O(4)	0.628 8(4)	0.442 4(4)	0.195 81(8)
N(1)	0.183 3(3)	0.099 9(3)	0.217 31(6)
N(2)	0.203 5(3)	0.088 9(3)	0.178 14(6)
N(3)	0.270 6(3)	0.423 0(3)	0.234 08(6)
N(4)	0.175 3(4)	0.499 7(4)	0.229 89(10)
C(1)	0.240 4(4)	0.049 2(4)	0.213 39(7)
C(2)	0.252 6(4)	0.040 5(4)	0.189 51(9)
C(3)	0.162 3(3)	0.121 9(3)	0.195 37(7)
C(4)	0.254 3(4)	0.430 3(4)	0.209 14(8)
C(5)	0.193 1(5)	0.476 4(5)	0.207 05(12)
C(6)	0.222 0(4)	0.465 7(4)	0.245 46(10)

At this stage ORTEP drawings of the asymmetric unit-cell contents suggested almost perfect 32 (D_3) symmetry, even extending to the thermal ellipsoid envelopes. However the additional three-fold axis was in an irrational direction perpendicular to *b* in the monoclinic cell. The cell dimensions were re-investigated and it was found that the transformation (½ ½ 1/0 0 1/½ — ½ 1) generated a rhombohedral cell within the limits of error, with the three-fold axis in the (111) direction of the new cell. Accordingly, the reflection data were reindexed to the corresponding hexagonal unit cell (by ½ ½ 0/ −½ ½ 0/1 0 3) and the monoclinic atomic co-ordinates transformed and averaged to the hexagonal setting of space group $R\bar{3}c$, which had the appropriate systematic absences. In this setting there are two independent silver atoms both in special positions (*x*, *x*, ¼) with symmetry 2. Further cycles of full-matrix least-squares refinement using the SHELX-76 system[15] converged with $R = 0.035$ [$R' = 0.046$ with $w = 1/(\sigma^2F + 0.015F^2)$]. The original reflection data were averaged to 2 049 reflections in $R\bar{3}c$ with an internal consistency index of $0.021 = \{\Sigma(N \times \Sigma\{w[F(\text{mean}) - F]^2\})/\Sigma[(N - 1) \times \Sigma(wF^2)]\}^{\frac{1}{2}}$, where the inner summations are over the *N* equivalent reflections averaged to give *F*(mean), and the outer summations are over all unique reflections. It was therefore concluded that $R\bar{3}c$ was in fact the correct space group, and the tables of structure factors, anisotropic thermal parameters, and hydrogen-atom parameters in Supplementary Publication No. SUP 22779 (13 pp.),* and the atomic co-ordinates in Table 1 refer to the hexagonal setting of $R\bar{3}c$.

TABLE 2

Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Ag(1)–Ag(2)	3.051(1)	Ag(1)–Ag(1)	3.493(1)
Ag(1)–N(1)	2.075(3)	Ag(2)–N(3)	2.089(3)
N(1)–C(1)	1.366(6)	N(3)–C(4)	1.400(5)
N(1)–C(3)	1.318(5)	N(3)–C(6)	1.302(6)
C(1)–C(2)	1.336(6)	C(4)–C(5)	1.352(8)
C(2)–N(2)	1.371(6)	C(5)–N(4)	1.354(8)
N(2)–C(3)	1.326(6)	N(4)–C(6)	1.325(7)
Cl(1)–O(1)	1.441(4)	Cl(1)–O(3)	1.424(3)
Cl(1)–O(2)	1.434(3)	Cl(4)–O(4)	1.417(4)
Ag(2)–O(1)	3.011(3)	Ag(2)–O(2)	2.926(3)
N(1)–Ag(1)–Ag(2)	89.2(1)	N(3)–Ag(2)–Ag(1)	88.4(1)
C(1)–N(1)–Ag(1)	129.3(3)	C(4)–N(3)–Ag(2)	126.8(3)
C(3)–N(1)–Ag(1)	125.7(3)	C(6)–N(3)–Ag(2)	126.8(3)
C(1)–N(1)–C(3)	105.0(3)	C(4)–N(3)–C(6)	106.4(4)
N(1)–C(1)–C(2)	110.4(4)	N(3)–C(4)–C(5)	107.1(5)
C(1)–C(2)–N(2)	105.7(4)	C(4)–C(5)–N(4)	107.2(4)
C(2)–N(2)–C(3)	107.4(4)	C(5)–N(4)–C(6)	108.0(4)
N(2)–C(3)–N(1)	111.4(4)	N(4)–C(6)–N(3)	111.2(5)

Mean of O–Cl–O angles 109.5°, standard deviation = 0.7°

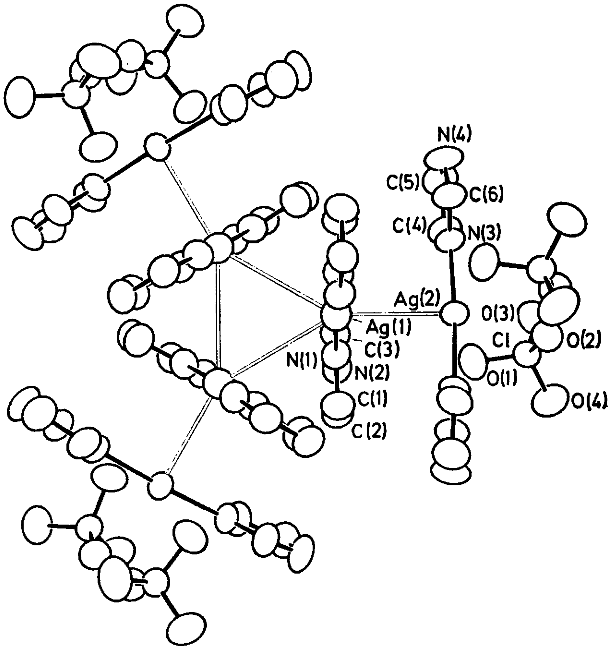

FIGURE 1 The hexamer unit observed in the crystal structure of $[\text{Ag(imid)}_2][\text{ClO}_4]$, viewed along the crystallographic three-fold axis. There are two-fold axes along each Ag(1)–Ag(2) vector. Hydrogen atoms are not shown, and the atom outlines are the 50% probability ellipsoids

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

Bond lengths and angles are given in Table 2.

Crystal structure of $[Ag(imid)_2][ClO_4]$. The basic structural unit consists of six linear $[Ag(imid)_2]^+$ cations, and six $[ClO_4]^-$ anions oriented as shown in Figure 1. The unit has crystallographic 32 (D_3) symmetry, with three Ag(1) ions forming an equilateral triangle of side 3.493(1) Å, and three Ag(2) ions radiating 3.051(1) Å out along the two-fold axis directions. The imidazole ligands and $[ClO_4]^-$ ions are oriented as shown in Figure 2. The torsion angle N(1)–Ag(1)–Ag(2)–N(3) * is 95.6°, and the bonds Ag(1)–N(1) and Ag(2)–N(3) are at 60.1° and 24.3° respectively to the plane through the silver atoms. There are two of these hexameric units in the rhombohedral unit cell, but there are no further Ag · · · Ag distances less than 5 Å.

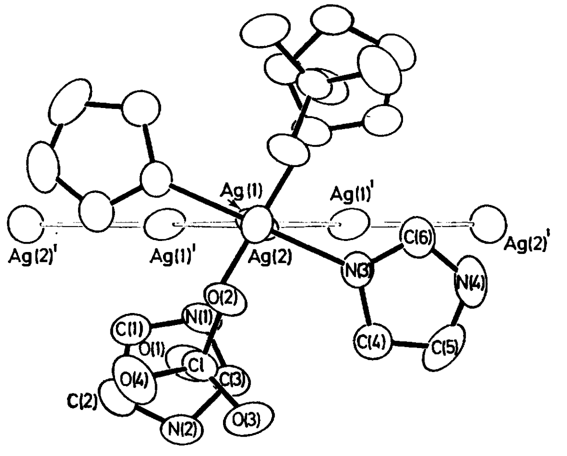

FIGURE 2 A projection along the Ag(2)–Ag(1) direction, showing only the imidazole and $[ClO_4]^-$ groups associated with one Ag(1) and one Ag(2) atom. Hydrogen atoms are not shown, atom outlines are 50% probability ellipsoids

There has been extensive discussion over what constitutes a bonding distance between silver atoms,[8,16] but in nearly every case the metal atoms are also bridged by other atoms. This is not the case in the structure of $[Ag(imid)_2][ClO_4]$; there seems to be a definite bonding interaction, not only at 3.051 Å between Ag(1) and Ag(2), but even at 3.493 Å between the Ag(1) atoms of the inner triangle. There is no other apparent reason for this aggregation of the $[Ag(imid)_2]^+$ ions; the imidazole rings adopt positions which appear to be minimising any possible mutual interaction, and the closest potential bridging distances Ag(1) · · · N(3) and Ag(2) · · · N(1) are 3.66 Å. This structure is also to be contrasted with that of $[Ag(imid)_2][NO_3]$ [8] which consists of isolated linear cations with no Ag · · · Ag distances less than 5.0 Å. However, one preparation of the perchlorate did produce a second phase which may well have been analogous to the nitrate (see below and Figure 3).

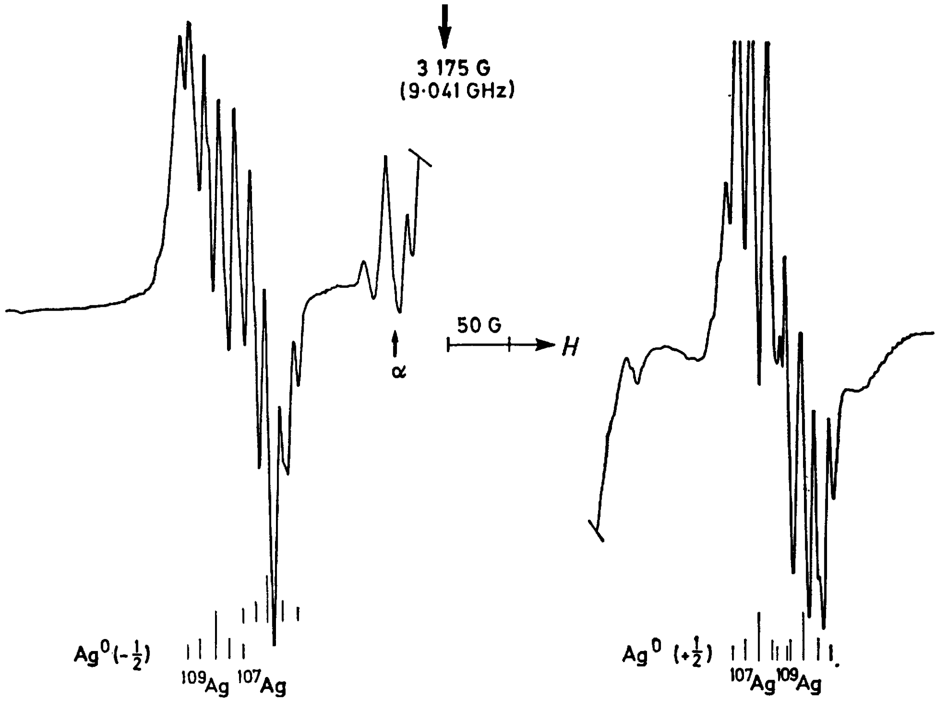

FIGURE 3 First derivative *X*-band e.s.r. spectrum for a minor crystalline modification of $[Ag(imid)_2][ClO_4]$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to an Ag^0 centre. Features α may be the perpendicular features for an Ag^{II} centre, but no parallel features have been detected

The imidazole rings are planar (see Table 3) and their geometry is in excellent agreement with that reported for $[Ag(imid)_2][NO_3]$.[8] The Ag(1)–N(1) distance is somewhat shorter than either Ag(2)–N(3) or the corresponding distances in the nitrate. The two $[ClO_4]^-$ ions take up positions on the periphery of the cluster, being associated with the Ag(2) atom and oriented so that two oxygen atoms of each $[ClO_4]^-$ are equidistant from it. The two chlorine atoms occupy, with Ag(1), the equatorial sites of a distorted trigonal bipyramid about Ag(2), atoms N(3) occupying the axial positions. Thus the Ag(1) atom is presumably in

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* As defined by R. H. Stamford and J. Waser, *Acta Cryst.*, 1972, **A28**, 213.

a slightly more positive environment than Ag(2), which may account for the shorter Ag(1)–N(1) distance.

There is no hydrogen bonding in the crystal structure, judged by intermolecular distances, the closest approach of a nitrogen or oxygen atom to hydrogen being 2.1 Å. This contrasts again with the corresponding nitrate structure, and is further supporting evidence that the cluster is held primarily by Ag · · · Ag interactions.

Electron Spin Resonance Results.—Most polycrystalline preparations and the single crystals gave e.s.r. spectra characteristic of a trimer centre. However, certain preparations gave a different crystalline modification whose e.s.r. spectrum, after irradiation, was dominated by features assigned to a monomeric Ag^0 centre (Figure 3). The $^{107/109}Ag$ hyperfine coupling is nearly isotropic, indicating *ca.* 69% occupancy of the 5*s* orbital. There is well defined coupling to two equivalent ^{14}N nuclei, the interaction again being nearly isotropic. These results clearly apply to a centre formed by electron addition to isolated $[Ag(imid)_2]^+$ cations, without loss of the ligands. The results are compared with those for a similar centre formed from $[Ag(NCMe)_4]^+$ ions, in Table 4.[6] The present centre shows a reduced isotropic coupling to silver, and an enhanced coupling to nitrogen. Since for the cyanomethane centre there is delocalisation onto four ligands, the total delocalisation is probably comparable. The remaining spin density is probably in the $4p_x$, $4p_y$ orbitals for the imidazole complex: anisotropic coupling from such population would be small, and probably not detectable under our conditions.

TABLE 3

Equations of least-squares planes of the imidazole rings (*x*, *y*, *z* are fractional crystal co-ordinates). Distances (Å) of atoms from the planes are given in square brackets

Ring (1): N(1), C(1), C(2), N(2), C(3)

$$6.873x + 7.562y + 1.240z = 2.285$$

[N(1) −0.000, C(1) 0.005, C(2) −0.007, N(2) 0.007, C(3) −0.005, Ag(1) 0.041]

Ring (2): N(3), C(4), C(5), N(4), C(6)

$$-6.409x - 7.992y + 2.378z = -4.563$$

[N(3) 0.004, C(4) −0.009, C(5) 0.010, N(4) −0.008, C(6) 0.002, Ag(2) 0.105]

Angles (°) between normals to Ag plane and Ring (1) = 88.7°; Ring (2) = 87.5°.

Angles (°) between the vector Ag(1)–Ag(2) and Ring (1) normal = 2.04; Ring (2) normal = 4.40.

TABLE 4

E.s.r. parameters for paramagnetic centres in $[Ag(imid)_2][ClO_4]$ and for related species

				g-tensor components		
Centre	Medium		Isotropic hyperfine coupling/G	∥	⊥	iso.
Ag^0	$[Ag(imid)_2][ClO_4]$ [a]	^{109}Ag	−485			1.998
		^{14}N	11.5 (2N)			
Ag_3^{2+}	$[Ag(imid)_2][ClO_4]$ [b]	^{109}Ag	*ca.* −110	*ca.* 1.96	1.99	*ca.* 1.98
		^{14}N	7.8 [c]			
Ag^0	$[Ag(NCMe)_4][ClO_4]$ [d]	^{109}Ag	−631			1.997
		^{14}N	6.5			
Ag_3^{2+}	Toluene [e]		−203			1.970

[a] For the minor crystal modification. [b] For the normal crystal modification. [c] $A_{\parallel} = 8.5$ G, $A_{\perp} = 7.5$ G. [d] Ref. 6. [e] Ref. 3.

Most crystalline preparations, corresponding to that used for crystal-structure determination, gave rise to an Ag_3^{2+} centre on irradiation. A typical powder e.s.r. spectrum at 77 K is shown in Figure 4. The main spectrum comprises four sets of features ($-\frac{3}{2}$, $-\frac{1}{2}$, $+\frac{1}{2}$, and $+\frac{3}{2}$ in Figure 4) characteristic of hyperfine coupling to three equivalent or almost equivalent silver nuclei. (^{109}Ag and ^{107}Ag, in almost equal abundance, have $I = \frac{1}{2}$ and very similar, negative magnetic moments.) It is characteristic of such spectra for the $M_I = \pm\frac{1}{2}$ components to be broader than the $\pm\frac{3}{2}$ components.[3] This arises largely because of the extra second-order splitting of these features, but it may also imply slight inequivalences in the perpendicular coupling constants. There is a clear difference between parallel and perpendicular components, which is unusual for the spectra of silver aggregates.[3] The multiplet structure stems from two factors, a 1 : 3 : 3 : 1 contribution from the different combinations of the three ^{109}Ag or ^{107}Ag nuclei, and a multiplet splitting from a range of equivalent nitrogen nuclei. The splitting between the ^{109}Ag–^{107}Ag features is calculated to be close to the observed splitting of 6.3 G,* and this fortuitously contributes to the good resolution of the outer ($\pm\frac{3}{2}$) features. The best fit to the defined lines is obtained for six equivalent ^{14}N nuclei.

We conclude that there is an unpaired electron attached to a trimer cluster, $\{Ag(imid)_2\}_3^{3+}$. The e.s.r. data are given in Table 4. The most notable differences between these results and those for the Ag_3^{2+} centre previously described are the presence of hyperfine coupling to six ligands, the marked shift in $g_{\parallel}$ to high fields, and the small value for A_{iso} (^{109}Ag) (*ca.* −110 G) compared with that previously observed (−203 G).

The major anisotropy is in the *g* tensor, with $g_{\parallel} < g_{\perp} < 2.002\,3$. Unfortunately, the low-field ($M_I = -\frac{1}{2}$) parallel feature is badly obscured by overlap with the more intense $-\frac{3}{2}$ and $-\frac{1}{2}$ perpendicular features and could not be accurately assigned. However, the $-\frac{1}{2}$ perpendicular features were always of slightly lower amplitude than the $+\frac{1}{2}$ features, which implies that $A_{\parallel} < A_{\perp}$ (^{109}Ag).

Structure of the electron adduct. The most surprising result is the complete absence of hyperfine interaction with three of the silver ions. Since the silver–silver distance in the pairs is short (Table 2) and since we are adding a single electron into the system, it is hard to understand why the wave function does not cover all six silver ions. We favour the three central ions as being responsible for the hyperfine coupling, but this is not certain. If we postulate a molecular orbital covering all six ions, the three outer ions could have a high spin density, provided the hyperfine coupling to the three central ions is small. Either way, absence of any contribution from the other three ions is most surprising, and we can offer no convincing explanation.

In order to explain the low value for $g_{\parallel}$, we need to postu-

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* Throughout this paper: 1 G = 10^{-4} T.

late occupancy of the in-plane $5p$ orbitals ($5p_x$ and $5p_y$). This must be considerable in view of the low value for $A_{iso.}$. Thus, the total $5s$ character is only *ca.* 0.55. Delocalisation onto the imidazole ligands may account for a further 0.25. If the remaining spin density is in a combination of the $5p_x$ and $5p_y$ orbitals the anisotropy in the hyperfine coupling would be small, but would require that $A_{\parallel} < A_{\perp}$, as we deduced to be the case. This result agrees qualitatively with the model, but we are unable to obtain a precise estimate of the $4p_{x,y}$ populations. It is noteworthy that the experimental value for $A_{\parallel}(^{14}N)$ is greater than that for $A_{\perp}(^{14}N)$. This result requires that the imidazole ligands lie relatively close to the parallel (z) axis. This is true for the inner silver ligands, but those for the outer set lie in the silver plane. Thus if the outer set bore the high spin density, $A_{\perp}(^{14}N)$ would have to be $>A_{\parallel}(^{14}N)$. This result seems to establish that it is indeed the inner three silver ions that accommodate the extra electron. We conclude that the e.s.r. parameters are well accommodated provided that the spin is confined to the inner three silver ions, but we are unable to explain why the outer three ions are excluded from this orbital. Possibly the weakly coordinated ClO_4^- ions reduce the electron affinity of the Ag(2) ions so much relative to Ag(1) that the electron prefers to remain on the Ag(1) group.

One curious additional result should be mentioned On warming above 77 K, the e.s.r. spectral features gradually moved apart without any concomitant broadening; this change was not caused by a partial motional averaging since the $-\frac{1}{2}$ perpendicular features moved to low field. The reversible change corresponds to an overall gain in $5s$ character on heating. We tentatively suggest that it is caused by a slight increase in the silver–imidazole bond lengths. This would reduce the occupancy of the $5s$ orbital by bonding electrons and hence the $5s$ character of the extra electron would increase.

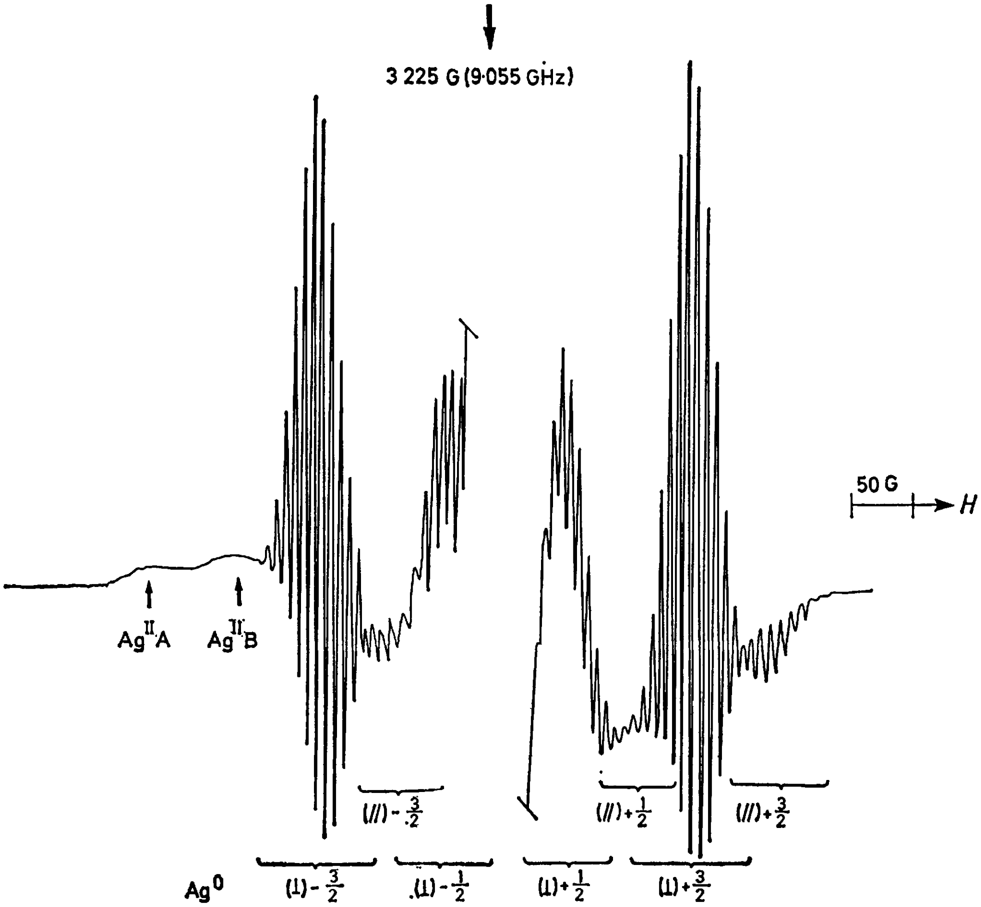

FIGURE 4 First derivative *X*-band e.s.r. spectrum for the normal form of $[Ag(imid)_2][ClO_4]$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to an Ag_3^{2+} centre. Features β are parallel features assigned to Ag^{II} centres

The Ag^{II} *centres.* Little can be said of these centres. For the normal crystals, only the parallel features are well defined. Two such features ($g_{\parallel} = 2.175$ and $g_{\parallel} = 2.131$) are observed with comparable intensities (Figure 4), but the separation (*ca.* 70 G) is too big for hyperfine coupling to $^{107/109}Ag$ nuclei, and we therefore suggest that two different Ag^{II} units are involved. This would be expected if both Ag(1) and Ag(2) ions can lose electrons with comparable facility. The perpendicular features undoubtedly occur on the low-field side of the free-spin region, but overlap with the $M_I = -\frac{1}{2}$ features for the Ag_3^{2+} centre and intense central free-radical features precluded analysis.

Despite the paucity of data, there are several aspects of these results that are of interest. One is that the form of the

g-tensor components, with $g_{\parallel} > g_{\perp} > 2.002\,3$, is characteristic of silver(II) complexes having a $3d_{x^2-y^2}{}^1$ configuration rather than a $3d_{z^2}{}^1$ configuration.[17] It might be supposed that the strong, near-linear bonding from the two imidazole ligands would constrain the ' hole ' within the σ^* regions giving a $3d_{z^2}{}^1$ type configuration (where z now refers to the N–Ag–N directions). This almost certainly occurs for the Ag^{II} centre formed in the minor crystalline form (Figure 3). Here there are no low-field parallel features, but a set of perpendicular features in the $g = 2.05$ region separated by *ca.* 18 G are almost certainly due to $[Ag(imid)_2]^{2+}$ ions with a $3d_{z^2}{}^1$ configuration. This requires that $g_{\perp} > g_{\parallel} \sim 2.002\,3$,[17] so we would not expect to be able to detect the parallel features. Clearly in this instance, bonding from the ClO_4^- ions is either too weak to influence the structure or it is such that the $3d_{z^2}$ orbital is still uppermost. This result is in marked contrast with our results for an Ag^{II} centre formed in the irradiated nitrate.[9] In this case, the favoured structure was unambiguously $3d_{x^2-y^2}{}^1$ and two ^{14}N nuclei gave well defined hyperfine coupling. We concluded that strong interaction with one or more nitrate ions in the xy plane containing the two imidazole nitrogen atoms must be present.

These considerations suggest that the ClO_4^- ions do not constrain the unpaired electron into a $3d_{x^2-y^2}$ type orbital for the normal crystalline form of the perchlorate. For the Ag(2) ions, bonding to Ag(1) might be enough to cause the change from $3d_{z^2}{}^1$ to $3d_{x^2-y^2}{}^1$, but this seems to us to be most surprising. Unfortunately, the low-field parallel features are not resolved, so we are unable to estimate the number of silver nuclei contributing to the coupling. It seems probable that the ' hole ' is delocalised onto more than one silver atom, but in the absence of better data this cannot be verified.

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