Electron-gain and -loss Centres in Irradiated Di-imidazolesilver(I) Nitrate †

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Exposure of powder and single-crystal samples of di-imidazolesilver(I) nitrate to ^{60}Co γ-rays at 77 K gives paramagnetic centres whose e.s.r. spectra are characteristic of NO_2 radicals formed by electron gain and silver(II) centres formed by electron loss. There is no evidence for electron capture at silver(II), nor for any significant damage to the imidazole ligands. The e.s.r. spectra for the silver(II) centre show hyperfine coupling to ^{109}Ag and ^{107}Ag, and also to two equivalent ^{14}N nuclei. The results suggest a major silver contribution from the $4d_{x^2-y^2}$ orbital, where x is the N–Ag–N direction. This establishes the presence of co-ordinated nitrate ligands in addition to the two imidazole ligands.

WHEN silver nitrate crystals are exposed to ^{60}Co γ-rays at 77 K the electron-loss centre is Ag^{II} and the electron-gain centre is NO_3^{2-}.[1,2] There was no appreciable yield of the alternatives, Ag^0 and NO_3, and the presence of a small doublet splitting of the NO_3^{2-} features from ^{107}Ag and ^{109}Ag clearly established that the equilibrium (1)

$$(Ag^+ \cdots NO_3^{2-}) \rightleftharpoons (Ag^0 \cdots NO_3^-) \qquad (1)$$

lies well to the left in these crystals. In contrast, solutions of silver nitrate in cyanomethane at 77 K gave a variety of electron-gain centres, including NO_3^{2-}, NO_2, and Ag^0.[2] The major electron-loss centre was Ag^{II}, but there was no evidence for ^{14}N hyperfine coupling from co-ordinated cyanomethane. In the hope of shedding some light on these evidently complex processes, we have studied the effect of high-energy radiation on the di-imidazole complex. In this compound, the two imidazole ligands are linearly co-ordinated to silver(I). Nitrate ions are also weakly co-ordinated to silver.[3]

EXPERIMENTAL

Di-imidazolesilver(I) nitrate was prepared from silver nitrate and imidazole in ethanol. Well defined crystals were obtained on slow evaporation. These were washed with methanol and dried *in vacuo* prior to cooling in liquid nitrogen and exposing to ^{60}Co γ-rays in a Vickrad source at a dose rate of *ca.* 2 Mrad h^{-1} for *ca.* 4 h.‡ Finely ground powders were treated similarly.

E.s.r. spectra were recorded on Varian E3 and E109 spectrometers at 77 K. Rotations about three orthogonal axes were made with crystals mounted on a Perspex rod, readings being taken every 5—10° as necessary. In order to study thermal changes, the powder samples were allowed to warm in the empty insert Dewar flask, and were recooled to 77 K whenever significant changes were observed in the e.s.r. spectra.

RESULTS AND DISCUSSION

The powder e.s.r. spectra showed that only two major paramagnetic centres are formed in this material at 77 K. One of these is unambiguously identified as NO_2, the principal components of the g and A tensors being typical for this centre.[4] For reasons previously given,[5] we think that this is the major electron-gain centre, probably formed by the reactions (2) and (3). The other centre had g and A parameters typical of silver(II), so the primary reaction is probably (4).

$$NO_3^- + e^- \longrightarrow NO_3^{2-} \qquad (2)$$

$$Ag^+ + NO_3^{2-} \longrightarrow AgO^- + NO_2 \qquad (3)$$

$$AgL_2^+ + NO_3^- \longrightarrow AgL_2^{2+} + NO_3^{2-} \qquad (4)$$

The e.s.r. features for the silver(II) centre were not changed on annealing, and hence it seems that any structural modifications induced on electron loss occur rapidly at this temperature.

One curious difference between the powder and single-crystal spectra should be noted. Analysis of the powder spectrum in the parallel (low-field) region requires two sets of lines, the apparent doublet splitting being *ca.* 53 G (Figure 1). We therefore provisionally assigned the multiplet splitting to a set of equivalent ^{14}N nuclei, and the doublet splitting to ^{109}Ag and ^{107}Ag. (^{109}Ag and ^{107}Ag have almost equal abundance, and their magnetic moments are so similar that their features would be superimposed under our conditions.) This assignment seemed to be supported by the fact that $A_{\parallel}(^{109}Ag) \approx 53$ G, which although large is nevertheless an acceptable result. However, the single-crystal spectra, for orientations close to parallel, showed no large doublet splitting (Figure 1), the ^{109}Ag–^{107}Ag coupling being *ca.* 4.3 G. As can be seen from Figure 1, the low-field lines of the powder spectrum tie in well with the crystal spectra. The high-field set seem to have no counterpart in the crystal spectra and we are unable to offer any compelling explanation. It may be that there is some pseudo-turning point that shows up fortuitously, but we know of no reason for this. However, if the extra set of features (in the powder spectrum) is not due to the species detected in the crystal samples there are an unusual number of coincidences, since the couplings to ^{109}Ag, ^{107}Ag, and ^{14}N are about the same. We tentatively suggest that surface sites are involved and that they experience a smaller g shift for reasons unknown to us. Analysis of both the single-crystal and powder spectra was impossible close to the perpendicular region because of overlap with the broad, intense, $\cdot NO_2$ features. However, sufficient data were measurable from the crystal

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† Taken as Unstable Intermediates Part 189.

‡ Throughout this paper: 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T.

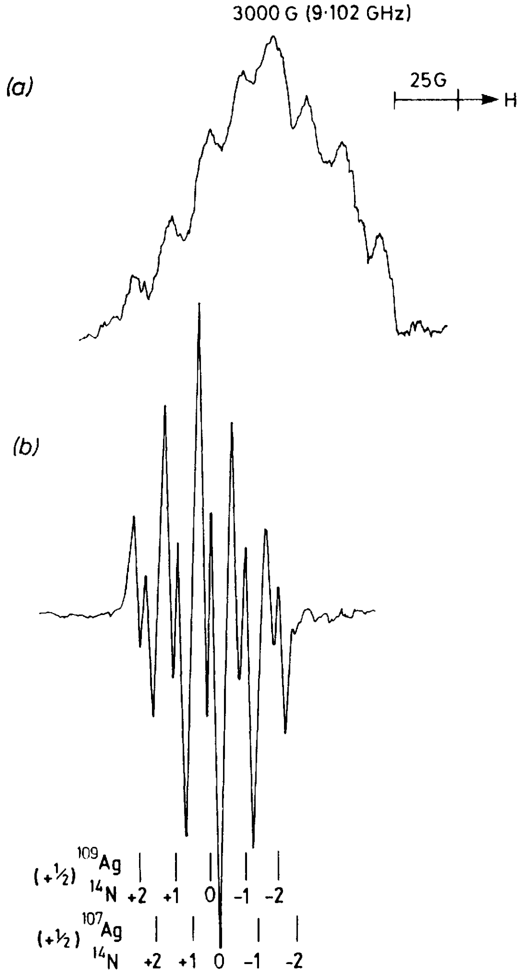


FIGURE 1 First-derivative X-band e.s.r. spectrum for (*a*) powdered and (*b*) single-crystal di-imidazolesilver(I) nitrate after exposure to ^{60}Co γ-rays at 77 K showing features assigned to the silver(II) centre, together with the extra features in (*a*) discussed in the text. Only the parallel region is shown

spectra to allow a good extrapolation using the usual theoretical equations for the angular dependence of the spectra.[6,7] The resulting theoretical curves fitted the experimental curves most satisfactorily (Figure 2). Also we were able to fit the powder spectrum with the resulting perpendicular parameters, which are given in Table 1.

TABLE 1

E.s.r. parameters for the silver(II) ion in irradiated di-imidazolesilver(I) nitrate together with data for similar silver(II) complexes

			Hyperfine coupling constants/G			
	g values		^{109}Ag [a]		^{14}N	
Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	$A_{\parallel}$	$A_{\perp}$
$Ag(imH)_2^{2+}$	2.217	2.035	(±) 4.6	(−) 18.1	20	15
$Ag(bipy)_2^{2+}$	2.210	2.047	(+) 42.2	(+) 26.0	30.1	21.1
$Ag(py)_2^{2+}$	2.178	2.050	(+) 16.4	(+) 24.0	33.3	24.0
$Ag(NO_3)_2^-$ [b]	2.283	2.058	(+) 42	(+) 30		
Ag^{II}–KCl [c]	2.193	2.035	(+) 38	(+) 30		

[a] Separate features for ^{109}Ag and ^{107}Ag were not resolved. [b] From ref. 3. [c] C. J. Delbecq, W. Hayes, M. C. M. O'Brien, and Y. N. Yuster, *Proc. Roy. Soc.*, 1963, **271**, 243.

Structure of the Silver(II) *Complex*.—Because of the strong linear co-ordination to two imidazole ligands,[3] the most reasonable first-order structure is one in which the unpaired electron is in an orbital comprising an anti-bonding combination of $3d_{z^2}$ from silver and two approximately sp^2 σ orbitals from nitrogen. The large hyperfine coupling to ^{14}N accords with this structure, but the form of the g-tensor components is wrong. The $4d_{z^2}$ formulation requires that g_z be close to the free-spin g value (2.0023) and that $g_x \approx g_y \gg 2.00$.[7] Our results show that one g value is $\gg$2.00, the other two being nearly equal and much closer to 2.00. This is the pattern expected, and normally found, for a $\cdots d_{z^2}{}^2, d_{x^2-y^2}{}^1$ configuration. Also the form of the silver hyperfine coupling accords more satisfactorily with the $d_{x^2-y^2}{}^1$ structure.[7]

This surprising result can be rationalised provided there is weak co-ordination of one or more NO_3^- ligands. Further insight into the structure can be obtained from an analysis of the silver hyperfine coupling. Because the g values deviate considerably from 2.0023 we need to allow for orbital magnetism before estimating d- and s-orbital character. We have done this using the equations (5) and (6) where the hyperfine coupling is in

$$A_{\parallel} = A + 2B(1 - \tfrac{7}{4}\Delta g_{\parallel} - \tfrac{3}{4}\Delta g_{\perp}) \tag{5}$$

$$A_{\perp} = A - B(1 + \tfrac{11}{4}\Delta g_{\perp}) \tag{6}$$

MHz.[7] The results are summarised in Table 2. The estimated coupling ($2B$) for unit population of a $4d$ orbital on silver is $\pm$44.5 G.[7] We therefore strongly favour the second set of data in Table 2 which gives a spin density of *ca.* 46% on silver, since the first set gives an unreasonably small spin density. If the orbital is $d_{x^2-y^2}$ then $2B$ should be positive and hence $A_{\text{iso.}}$ is negative (−19.6 G) corresponding to positive spin density. (Note: the magnetic moments for ^{109}Ag and ^{107}Ag are negative.) This is unusual since the isotropic coupling generally stems from inner s-shell polarisation which leads to a negative spin density. For this to

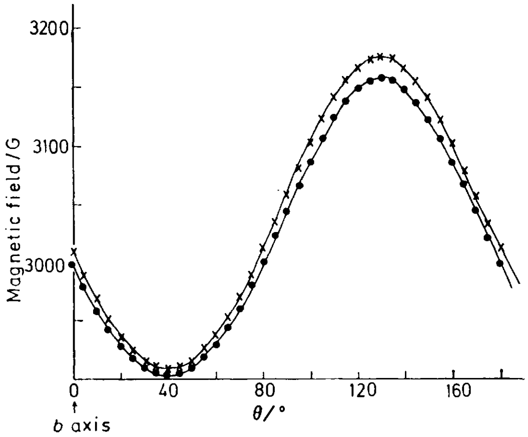


FIGURE 2 An example of the agreement between experimental field positions of the $M_I = \bullet\frac{1}{2}$ features for Ag^{II} (×) and the angular dependence predicted from the data in Table 1 (●)

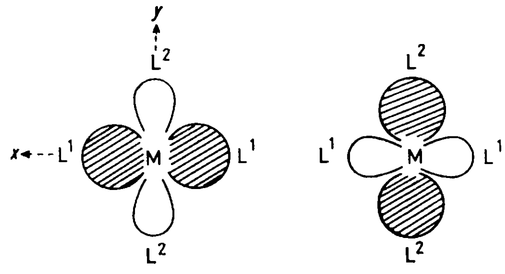
TABLE 2

Sets of possible ^{109}Ag hyperfine parameters obtained by correcting for orbital magnetic effects using equations (1) and (2)

$A_{iso.}$/MHz (G)	$2B$/MHz (G)	a_{4d}^{2} [a]	a_{5s}^{2} [b]
±25.2 (±9.0)	±32.4 (±11.6)	±0.26	0.013
±54.9 (±19.6)	±57.3 (±20.4)	±0.46	0.028

[a] 4*d* orbital population obtained from $2B$, using the unit population value of −124.6 MHz. [b] 5*s* orbital population obtained from $A_{iso.}$ using the unit population value of −1 960 MHz.

become positive, we need a relatively large admixture of the outer 5*s* orbital. [If the normal polarisation value is taken as *ca.* −25 G, then we require a contribution of $(19.6 + 25)/700 = 0.064$ from 5*s* to give +19.6 G.] This admixture is normally forbidden for a $\cdots d_{x^2-y^2}{}^1$ structure, but becomes allowed if the bonding along the *x* axis differs from that along *y*, and indeed serves a useful purpose, as can be judged from (I) and (II). If bonding to L^1 is stronger than that to L^2, the bonding σ orbital will be augmented along *x*, as in structure (I), whilst the antibonding orbital will be augmented along *y* (II). Hence the orbital shown in (II) will be occupied by the unpaired electron, thereby reducing the spin density on L^1, and favouring L^2. This fits the imidazole structure very well provided there are two weakly bound nitrate ions close to the *y* axis. (It is interesting to note that four weakly bound L^2 ligands along *y* and *z* would result in a new structure in which the unpaired electron would favour a d_{x^2} type orbital, or d_{z^2} when *z* is redefined along the imidazole–silver direction.) It is this relatively large 5*s* admixture that makes the hyperfine coupling to ^{109}Ag and ^{107}Ag different from the usual results for silver(II) complexes.



(I) (II)

The spin density on the two imidazole nitrogen atoms can also be estimated approximately from the ^{14}N coupling constants. (The indirect orbital and dipolar contributions are small and are ignored here.) Using the data in Table 1 and the normal unit population values,[7] we find $16/550 = 0.029$ for the 2*s* population and $4/33 = 0.12$ for the $2p_\sigma$ population. This gives a total density on the imidazole ligands of *ca.* 0.3% which is reasonable for the proposed structure. (In view of the approximations made and the small value of the anisotropic coupling, we estimate an error of *ca.* ±0.08 in this value.) The remaining spin density is presumably on the nitrate ligands.

Comparison with Other Silver(II) *Complexes*.—Some other results are summarised in Table 1. In particular, we draw attention to the results for $Ag(py)_2{}^{2+}$ (ref. 8) and $Ag(bipy)_2{}^{2+}$ [9] where py = pyridine and bipy = 2,2′-bipyridyl. The results for $Ag(bipy)_2{}^{2+}$ show that the expected $\cdots d_{x^2-y^2}{}^2$ configuration is favoured, but only two equivalent nitrogen ligands involved in the σ* orbital were detected. In this case $A_{iso.}(^{109}Ag)$ is positive so that spin polarisation is involved and there is no significant admixture of the 5*s* orbital. It seems probable that, in aqueous nitric acid, both bipy ligands are monoprotonated.[10]

Hyperfine coupling to only two ^{14}N nuclei was also observed for $Ag(py)_2{}^{2+}$.[8] It is noteworthy that in this case $A_{\parallel}(^{109}Ag)$ is considerably reduced, which is most readily explained in terms of some 5*s* admixture, as for the imidazole complex. In fact, the authors [8] proposed a $\cdots d_{z^2}{}^1$ structure for this complex, presumably because of the known linear co-ordination of the two pyridine ligands. In our view, the results, which are remarkably similar to those for the $Ag(bipy)_2{}^{2+}$ complex, preclude this assignment, and establish that the configuration remains $\cdots d_{x^2-y^2}{}^1$. Thus we again need to postulate the presence of weakly bound ligands (water or nitrate ions) along the *y* axis [as in (II)], with 5*s* admixture to give the required distortion of the wavefunction.

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REFERENCES

[1] W. C. Mosley and W. G. Moulton, *J. Chem. Phys.*, 1965, **43**, 1207.

[2] D. R. Brown, T. J. V. Findlay, and M. C. R. Symons, *J.C.S. Faraday I*, 1976, 1792.

[3] C.-J. Antti and B. K. S. Lundberg, *Acta Chem. Scand.*, 1971, **25**, 1758.

[4] J. H. Sharp and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 3075.

[5] M. C. R. Symons and D. N. Zimmerman, *J.C.S. Faraday I*, 1976, 409.

[6] A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions,' Oxford University Press, London, 1970.

[7] M. C. R. Symons, 'Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy,' Van Nostrand–Reinhold, London, 1978.

[8] T. Halpern, W. D. Phillips, and J. A. McMillan, *J. Chem. Phys.*, 1970, **52**, 5548.

[9] T. Halpern, S. M. McKoskey, and J. A. McMillan, *J. Chem. Phys.*, 1970, **52**, 3526.

[10] H. N. Po, *Co-ordination Chem. Rev.*, 1976, **20**, 171.