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Preliminary communication

A PARAMAGNETIC SILVER-CYANOMETHANE DERIVATIVE

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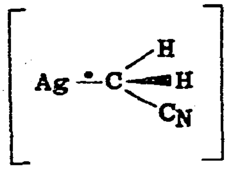
SUMMARY

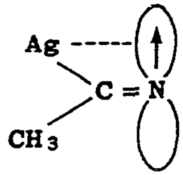
The e.s.r. spectrum of a silver(0)cyanomethane complex is described, the structure of which resembles that of an imino radical.

In view of the recent discovery of novel paramagnetic silver-ethylene and silver-acetylene complexes [1] we thought it would be of interest to report our identification of a silver-cyanomethane complex having rather similar properties. Kasai's preparative procedure is to co-condense silver atoms and the organic substrate in a rare-gas matrix at 4.2 K. Our method is to dissolve silver perchlorate in cyanomethane or cyanomethane + cosolvent, freeze to 77 K and expose to γ-rays. In our case a variety of magnetic centres are formed including Ag(II), [2] Ag(0) [2], $H_2\dot{C}CN$ and $(CH_3CN)_2^-$ [3], in addition to the centre of interest, whose e.s.r. spectrum is shown in Fig. 1. This comprises a major doublet (180G) clearly due to hyperfine coupling to ^{109}Ag and ^{107}Ag, and a set of parallel features interpreted in terms of ^{14}N hyperfine coupling.

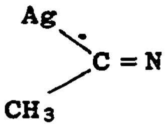
The yield of this species was enhanced on annealing above 77 K when the concentration of organic radicals began to fall, and we suggest



(I)



(II)



(III)

that it is formed either from $\cdot CH_2CN$ or from $CH_3\dot{C}N^-$ radicals to give I or II. Of these, we strongly favour structure II (III is an alternative extreme formulation for this radical). One reason for this preference is the large $A_{\parallel}(^{14}N)$ coupling. Radical I should have the

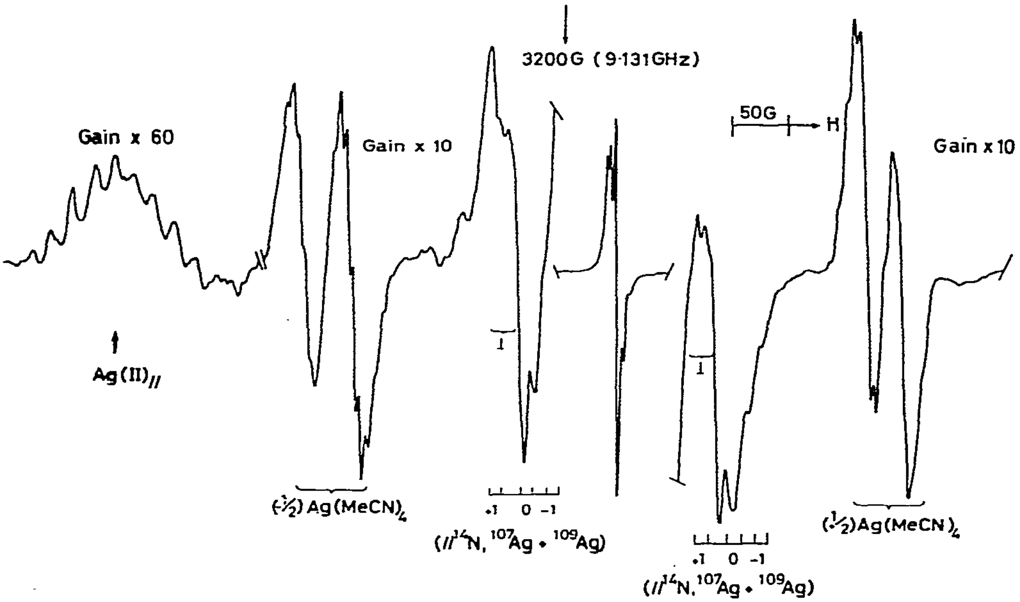
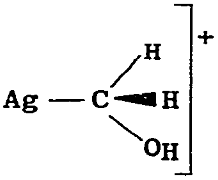
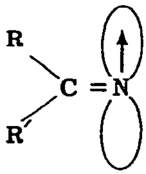


FIGURE. First derivative X-band e.s.r. spectrum for $AgClO_4$ in cyanomethane (CD_3CN + CD_3OD) after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the silver-imino radical (A) together with features assigned to Ag(0) and Ag(II) centres and central features from solvent radicals.

unpaired electron quite strongly confined to the Ag---C σ orbital, and spin-density on ^{14}N should be very small. Also, the structurally comparable radical IV has been prepared from $\cdot CH_2OH$ radicals [4], and this has $A(^{109}Ag) = 110$ G, which is significantly less than the coupling assigned to the cyanomethane derivative. The $A/$ (^{14}N) coupling (28 G) is close to that observed for structurally similar imino radicals (V)



(IV)

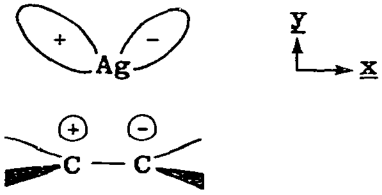


(V)

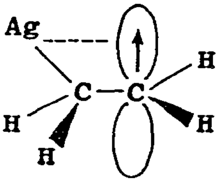
(usually in the region of 32 G [5]). Also, the $5s$ spin-density on silver, calculated from the isotropic hyperfine coupling, is *ca*. 0.25, and can be compared with the value of 0.17 derived from the ^1H hyperfine coupling for V having $R = H$ [5]. These values are remarkably similar, considering the great difference between hydrogen and silver. They imply that silver is somewhat less electronegative than hydrogen.

When considering the structures of $H_2C\dot{N}$ and related species, it is usual to invoke the theory of hyperconjugation or σ-π delocalisation in order to explain the large proton hyperfine coupling [6]. The same theory can clearly be used to explain the ^{109}Ag and ^{107}Ag coupling for $AgMeC\dot{N}$. Since, in this case, the σ^* structure III is an acceptable alternative of which there are a variety of examples, we feel that this provides an example which nicely explores the limiting structures involved in hyperconjugation. Also, so far as we are aware, it is the first example in which a metal substituent exhibits a large hyperconjugative interaction in a radical.

The contrast with the results for the Ag---ethylene complex is most marked. In this case the $5s$ (Ag) character of the unpaired electron was very small, and a symmetrical structure (VI) was proposed in which its unpaired electron is mainly in a non-bonding orbital $[b(4d_{xy}) -a (5p_x)]$:



(VI)



(VII)

Had the more familiar asymmetric addition occurred to give (VII) the silver atom would have been in a strongly hyperconjugative site and would have been expected to exhibit an isotropic hyperfine coupling comparable with that for II.

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