

Electron and Hydrogen Atom Addition to the Tetracyanoplatinate(II) Ion: an E.S.R. Study

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Summary Hydrogen atoms generated by γ -radiolysis of aqueous sulphuric acid matrices at 77 K add to $\text{Pt}(\text{CN})_4^{2-}$ ions to give $[\text{H}^-\text{Pt}(\text{CN})_4]^{2-}$ ions, the unpaired electron being in a σ^* orbital confined to hydrogen (*ca.* 35%) and platinum; electron addition followed by proton addition in methanol matrices gave the same complex.

We have recently suggested that a species formed during the γ -radiolysis of $\text{Ba}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ at 77 K having a large ^1H hyperfine coupling (*ca.* 150 G) is $\text{H}^-\text{Ni}(\text{CN})_4^{2-}$, having the unpaired electron in a σ^* orbital with a spin-density of *ca.* 0.3 on hydrogen.¹ This result is novel in that the ^1H hyperfine coupling is an order of magnitude greater than

those previously observed for hydrido ligands in transition-metal complexes. Furthermore, the excess electron acts as a probe of the metal-hydrogen σ -bond, and clearly establishes its strongly covalent character. It seemed of interest to find other systems in which such bonding occurs and, in particular, to obtain direct information about the metal contribution from its hyperfine coupling constants. (This was impossible for the nickel complex because of the very low abundance of ^{61}Ni .)

Exposure of solutions of $\text{K}_2\text{Pt}(\text{CN})_4$ in methanol at 77 K gave a variety of novel paramagnetic complexes. One major species is clearly the expected d^9 complex, but there appeared to be two other major species, both resembling d^7 complexes and both exhibiting large proton hyperfine

TABLE. Corrected e.s.r. parameters for $\text{H}^- \text{Pt}(\text{CN})_4^{2-}$ and $\text{D}^- \text{Pt}(\text{CN})_4^{2-}$ in various media.

Solvent	$A_{\parallel}^{195\text{Pt}}/\text{G}^a$	$A_{\perp}^{195\text{Pt}}/\text{G}$	$g_{\parallel}\text{Pt}$	$g_{\perp}\text{Pt}$	$2B/\text{G}$	A_{180}/G	$A^2\text{H}/^1\text{H}$
$\text{CD}_3\text{OD}-\text{D}_2\text{O}$	451	128	1.987	2.107	233	209	27
6 M- D_2SO_4	470	148	1.986	2.102	230	230	27
$\text{CD}_3\text{OD}-\text{D}_2\text{O}-\text{TMPD}$	451	130	1.986	2.106	231	210	27
6 M- H_2SO_4	474	146	1.985	2.102	234	230	180
MeOH	450	128	1.985	2.104	233	206	175
6 M- H_3PO_4	469	146	1.986	2.103	231	228	181

^a $G = 10^{-4} \text{ T}$.

couplings (*ca.* 175 G). When CD_3OD or $\text{D}_2\text{O} + \text{D}_2\text{SO}_4$ matrices were used, two sets of triplets were obtained (Figure). The change in splitting for the doublets and triplets was exactly that predicted for ^1H and ^2H hyperfine coupling. For the sulphuric acid systems the low-field set (doublets or triplets) are almost isotropic, whilst for methanolic systems they exhibit perpendicular and parallel components. The second intense set are clearly perpendicular components. The parallel sets were not completely resolved, but their high-field components were well defined. Approximate g_{\parallel} values were obtained on the assumption that, as with the nickel complex, the ^1H and ^2H coupling was almost isotropic.

These results were puzzling on two counts, one being that we were unable to formulate two quite different structures for species containing one strongly coupled hydrogen ligand, and the other being the apparent absence of any satellite features from ^{195}Pt flanking the perpendicular components (^{195}Pt has $I = \frac{1}{2}$, $\mu_N = 0.6004$ and is 33.7% abundant). These difficulties are both overcome if we postulate that the low-field set is due to complexes containing ^{195}Pt , there being only one type of complex present. (This is indicated in the Figure.) At first sight this seems unlikely since the intensities of these features are about equal to those of those from complexes containing non-magnetic platinum. However, provided $A_{\parallel}^{195\text{Pt}} \gg A_{\perp}^{195\text{Pt}}$ this difficulty is overcome. A careful search for the $M_I = -\frac{1}{2}$ (^{195}Pt) component associated with the parallel features was successful, as shown in the Figure. These features confirm the isotropic character of the ^2H hyperfine coupling. Calculation using the appropriate spin Hamiltonian shows that the $M_I = +\frac{1}{2}$ component should indeed appear close to the low-field set of lines. Thus, fortuitously, the $M_I = +\frac{1}{2}$ parallel and perpendicular features almost coincide, thus accounting for their disproportionately high intensities. The key to understanding this spectrum is that the parallel and perpendicular components for $M_I = +\frac{1}{2}$ set cover a very small field range (*ca.* 20 G), the central non-magnetic components cover a large field range (*ca.* 180 G), whilst the $M_I = -\frac{1}{2}$ components cover a very large range (*ca.* 330 G). Since the intensities of the turning-point features of the first-derivative power spectra are directly proportional to field range spanned by each component, the $+\frac{1}{2}$ set are very intense and the $-\frac{1}{2}$ set are very weak. Parameters derived from these species in various media are given in the Table.

On slight annealing, the d^9 complex $[\text{Pt}(\text{CN})_4^{2-}]$ in methanol was lost, and the features assigned to the $\text{H}^- \text{Pt}(\text{CN})_4^{2-}$ complex grew proportionately. Clearly these anions are strongly basic relative to methanol. It is noteworthy that $\text{Ni}(\text{CN})_4^{2-}$ ions were not protonated under these conditions. When solutions containing tetramethyl-*p*-phenylenediamine (TMPD) were photolysed to give electrons and $(\text{TMPD})^+$, similar results were obtained, thereby supporting our assignments.

Irradiation of glassy solutions in 6 M- $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ or $\text{D}_2\text{SO}_4-\text{D}_2\text{O}$ gave the hydrido complex in high yield, with suppression of the normal H^\cdot or D^\cdot yield. These results establish that the hydrido complex can be formed either directly by hydrogen atom addition, or, indirectly, by electron addition and protonation.

Analysis of the ^{195}Pt hyperfine coupling in the usual way must be preceded by subtraction of the orbital magnetic contribution.² When this is done, we obtain the data given in the Table. Since the form of the g -tensor establishes that the electron is in a $5d_z$ orbital on platinum, the

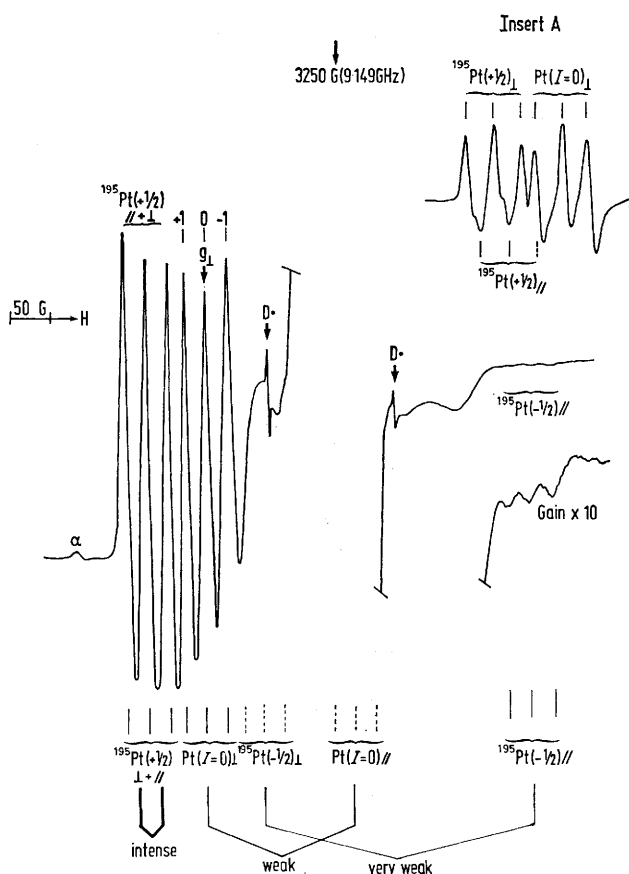


FIGURE. First-derivative X-band e.s.r. spectrum for a dilute solution of $\text{K}_2\text{Pt}(\text{CN})_4$ in $\text{D}_2\text{SO}_4-\text{D}_2\text{O}$, showing features assigned to the $\text{D}^- \text{Pt}(\text{CN})_4^{2-}$ complex. Central features due to matrix radicals have been omitted. The low-field feature α is due to $\text{H}^- \text{Pt}(\text{CN})_4^{2-}$ in low yield. Insert A gives the low-field section for the $\text{D}^- \text{Pt}(\text{CN})_4^{2-}$ complex in CD_3OD .

anisotropic coupling must be positive and, therefore, the isotropic coupling is positive. Hence, as is usually the case for such σ^* species, there is a considerable admixture of 6s (Pt) character. The spin densities on Pt estimated from the $5d_{z^2}$ coupling using the wavefunctions of Froese^{2,3} is *ca.* 0.83. When the wavefunctions of Herman and Skillman⁴ are used, we obtain *ca.* 0.77. Considering the inaccuracies involved for elements of high atomic number, agreement with the more accurate results derived from

the ^1H coupling is reasonable. We conclude that the unpaired electron is closely confined to hydrogen and platinum, with some preference for platinum. Hence the bonding σ -electron pair must have a comparable preference for hydrogen, which therefore has definite hydride ion character.

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⁴ F. Herman and S. Skillman, 'Atomic Structure Calculations,' Prentice-Hall, Englewood Cliffs, New Jersey, 1963.