Electron Spin Resonance Data for the Hydrogen–Transition Metal Bond in the Complex $[\text{HNi(CN)}_4]^{2-}$

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Summary Addition of hydrogen atoms to $[\text{Ni(CN)}_4]^{2-}$ ions in various salt hydrates induced by radiolysis gave $[\text{H}\dot{-}\text{Ni(CN)}_4]^{2-}$ ions in which the σ^* electron is strongly delocalised onto hydrogen $[A(^1\text{H}) = 150\ \text{G}]$.

As part of our e.s.r. studies of paramagnetic transition metal cyanides[1] and carbonyls,[2,3] we have endeavoured to prepare complexes in which the unpaired electron is in the metal–hydrogen σ^* orbital. This is because the ligand hyperfine coupling for such systems normally gives a good measure of the spin density on the ligand, as was found, for example, in our studies of $[(\text{CO})_5\text{Mn}\dot{-}\text{X}]^-$ (X = halide) anions.[3] This quest has been successful in studies of the radiolysis of systems containing the $[\text{Ni(CN)}_4]^{2-}$ ion, the yield being particularly high in $Ba[Ni(CN)_4]\cdot 1H_2O$. The Figure shows a Q-band e.s.r. spectrum obtained from this material after exposure to ^{60}Co γ-rays at 77 K. Another major nickel centre obtained in these studies was $[Ni(CN)_4]^{3-}$, having the unpaired electron in the σ^* $d_{x^2-y^2}$ orbital with considerable delocalisation onto the four cyanide ligands as evidenced by large ^{13}C hyperfine interaction to four equivalent carbon atoms. The third major product was $[Ni(CN)_4]^-$ whose g-tensor components were characteristic of complexes with a $\cdots d_{z^2}^1$ configuration. This result is perhaps surprising since the planar $[Ni(CN)_4]^{2-}$ ions are generally stacked so as to give relatively short Ni $\cdots$ Ni distances, there being no evidence for ligands in the 5th and 6th positions.[4] Probably some distortion occurs after electron loss which stabilises this configuration. Indeed this must be the case for the potassium salt $K_2[Ni(CN)_4].1H_2O$ since well defined hyperfine coupling to ^{14}N was detected, indicating bonding to nitrogen along the z-axis.

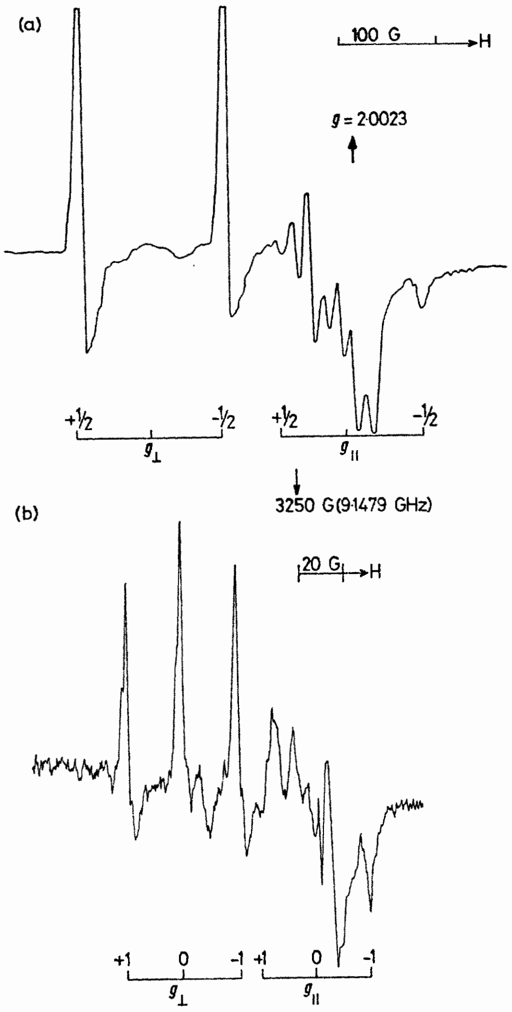

FIGURE. E.s.r. spectra assigned to $[HNi(CN)_4]^{2-}$: (a) first derivative Q-band spectrum for $Ba[Ni(CN)_4].H_2O$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[HNi(CN)_4]^{2-}$ ions; and (b) first derivative X-band spectrum for $Ba[Ni(CN)_4]$-D_2O after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[DNi(CN)_4]^{2-}$.

For $[H\dot{-}Ni(CN)_4]^{2-}$, the form of the g-tensor components is characteristic of a $\cdots d_{z^2}^1$ configuration on nickel, and the small shift in $g_\perp$ ($g_\perp = 2{\cdot}05$, $g_\parallel = 2{\cdot}00$) shows that the d_{z^2} orbital is well removed from the d_{xz}, d_{yz} π-levels relative to the simple $[Ni(CN)_4]^-$ ions. This indicates strong metal–hydrogen bonding. This is confirmed by the magnitude of the ^1H hyperfine coupling, which indicates a spin-density of *ca.* 30% on hydrogen. After allowing for some delocalisation onto the cyanide ligands, this result suggests that the unpaired electron is fairly evenly distributed within the σ^* orbital and hence that the H–Ni bond is strongly covalent. In other e.s.r. studies of complexes containing hydrogen as a ligand of which we are aware, the ^1H coupling has been relatively small, and characteristic of spin-polarisation rather than σ-delocalisation. Results for complexes such as $[AgH]^+$, which show similar extensive delocalisation onto hydrogen, are not directly comparable, since bonding is σ not σ^* and d orbitals are not involved.[5]

The anion $[HNi(CN)_4]^{2-}$ has been postulated as an intermediate in the radiolysis of aqueous solutions of $[Ni(CN)_4]^{2-}$ ions.[6] An intense band at *ca.* 360 nm was assigned to this species on mechanistic grounds, but the structure was not considered.

(*Received*, 12*th October* 1978; *Com.* 1103.)

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[1] See, *e.g.*, M. C. R. Symons and J. G. Wilkinson, *J.C.S. Dalton*, **1972**, 1086; **1973**, **14**, 965.

[2] See, *e.g.*, S. A. Fieldhouse, B. W. Fullam, G. W. Neilson, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 567; O. P. Anderson, S. A. Fieldhouse, C. E. Forbes, and M. C. R. Symons, *J. Organometallic Chem.*, 1976, **110**, 247.

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[6] Q. G. Mulazzani, M. D. Ward, G. Semerano, S. S. Emmi, and P. Giordani, *Internat. J. Radiation Phys. Chem.*, 1974, **6**, 187.