

## Structure of the $[\text{RhH}(\text{CN})_5]^{3-}$ Ion: an X-Ray and $^{13}\text{C}$ N.M.R. Study

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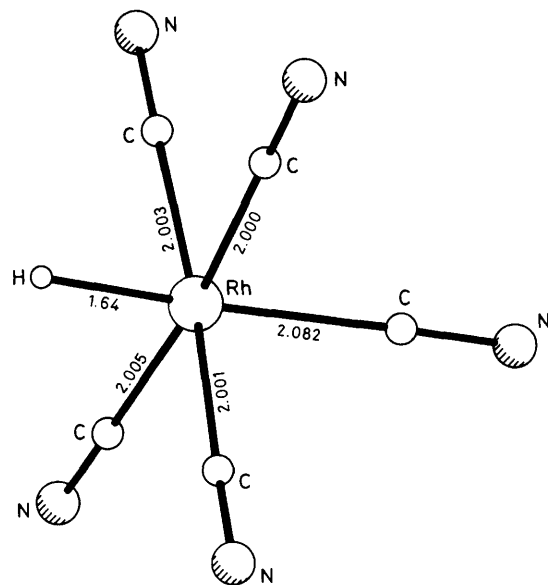
An X-ray single-crystal study of  $\text{K}_3[\text{RhH}(\text{CN})_5]\cdot\text{H}_2\text{O}$  confirms the nature of the octahedral hydrido complex anion; a  $^{13}\text{C}$  n.m.r. study shows that this structure is maintained in aqueous solution.

Cyanide hydride complexes are relatively rare species and there are no X-ray studies on them. The nature of the cyanide hydride complex of rhodium, made by reaction of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  with excess of methanolic KCN, has been variously reported to yield *trans*- $\text{K}_2[\text{RhH}(\text{CN})_4(\text{H}_2\text{O})]^\dagger$  and  $\text{K}_3[\text{RhH}(\text{CN})_5]\cdot\text{H}_2\text{O}$ .<sup>2</sup> The present studies show unequivocally that the product is, in fact,  $\text{K}_3[\text{RhH}(\text{CN})_5]\cdot\text{H}_2\text{O}$ , and that the structure of the anion is maintained in aqueous solution.

Crystals of  $\text{K}_3[\text{RhH}(\text{CN})_5]\cdot\text{H}_2\text{O}$  were prepared by the literature method<sup>1</sup> and recrystallized from water-methanol under argon. The crystal used for X-ray work was coated with picture varnish to prevent decomposition.

*Crystal data:*  $\text{K}_3[\text{RhH}(\text{CN})_5]\cdot\text{H}_2\text{O}$ , triclinic,  $a = 7.889(2)$ ,  $b = 8.677(2)$ ,  $c = 8.891(2)$  Å,  $\alpha = 88.91(2)$ ,  $\beta = 86.18(2)$ ,  $\gamma = 82.12(2)^\circ$ ,  $U = 601.5$  Å<sup>3</sup> (at 19°C), space group  $P\bar{1}$ ,  $Z = 2$ . X-Ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an  $\omega$  scan technique with graphite monochromated  $\text{Cu-K}\alpha$  radiation. A total of 1631 independent reflections were measured (to  $\theta = 57^\circ$ ), of which 105 were 'unobserved'. The structure was solved by Patterson and Fourier methods, and least-squares refinement has now reached  $R = 0.0235$ .<sup>†</sup> The program system SHELXTL<sup>3</sup> was used throughout the calculations, and the procedures described in ref. 4 were used to help confirm the position of the hydride hydrogen atom derived from least-squares refinement.

Figure 1 shows the structure of the title anion. There is a

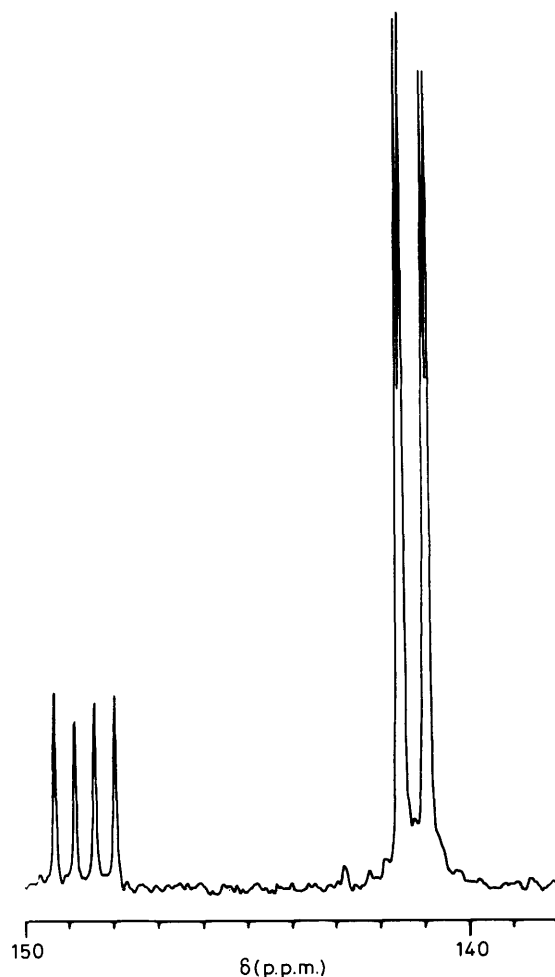


**Figure 1.** Structure of the  $[\text{RhH}(\text{CN})_5]^{3-}$  ion. Estimated standard deviations are Rh-C, 0.004; Rh-H, 0.04 Å.

<sup>†</sup> The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

slight distortion of the octahedral geometry in that the four equatorial cyanide groups are moved towards the hydrogen atom, such that the mean C(axial)-Rh-C(equatorial) angle is  $92.5^\circ$ . The Rh-C distance *trans* to the hydrido ligand is 2.082(4) Å, while the four equatorial Rh-C distances, which are all closely similar, average 2.002 Å. This lengthening of ca. 0.08 Å presumably indicates the higher *trans* influence of H as compared to the cyanide ligand. The Rh-H distance of 1.64(4) Å is in the range found for transition metal-H terminal bonds.<sup>5</sup>

The  $^1\text{H}$ -coupled  $^{13}\text{C}$  n.m.r. spectrum of an aqueous solution of  $[\text{RhH}(\text{CN})_5]^{3-}$  (unenriched) is shown in Figure 2 and is fully consistent with the structure in Figure 1. Two sets of doublets are observed. One set at  $\delta$  149 p.p.m. (*vs.* sodium 3-trimethylsilylpropanesulphonate; DSS) arises from the CN-group *trans* to the hydride whilst that at  $\delta$  141 p.p.m., which is four times more intense, arises from the four *cis* cyanide ligands. These doublets of doublets collapse to doublets on



**Figure 2.**  $^{13}\text{C}$  (62.9 MHz)  $^1\text{H}$  Coupled n.m.r. spectrum ( $\delta$  with respect to DSS; with external  $\text{D}_2\text{O}$  lock) of  $[\text{RhH}(\text{CN})_5]^{3-}$  in aqueous solution.

proton decoupling. Coupling between  $^{103}\text{Rh}$  (100% abundant,  $I = \frac{1}{2}$ )- $^{13}\text{C}$  and  $^{13}\text{C}$ - $^1\text{H}$  gives rise to the observed spectrum. The coupling constants are  $J(^{103}\text{Rh}, ^{13}\text{C})$  34.5;  $J(^{13}\text{C}, ^1\text{H}_{\text{trans}})$  56.6; and  $J(^{13}\text{C}, ^1\text{H}_{\text{cis}})$  5.7 Hz, the latter two being in agreement with those previously obtained from the  $^1\text{H}$  n.m.r. spectrum of a  $^{13}\text{C}$  enriched sample.<sup>6</sup>

The same spectrum is observed in excess of aqueous cyanide. An extra peak at  $\delta$  167 p.p.m. is due to free cyanide, its sharpness indicating that no exchange occurs. No extra resonances attributable to *trans*- $[\text{RhH}(\text{CN})_4\text{H}_2\text{O}]^{2-}$  are observed.

We thank the S.E.R.C. for the diffractometer system and for a grant to one of us (M. J. M.), and Mr R. N. Sheppard and Sue Johnson for obtaining the  $^{13}\text{C}$  n.m.r. spectra. We thank Johnson Matthey Ltd. for the loan of rhodium trichloride.

Received, 19th December 1983; Com. 1638

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