

## Cationic Ruthenium Ammine Complexes of Cyanotrihydroborate and of Hydrogen Cyanide

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**Summary** The synthesis and properties of the cationic complex cyanotrihydroboratopenta-ammineruthenium(II),  $[\text{Ru}(\text{NH}_3)_5(\text{BH}_3\text{CN})]^+$ , acid hydrolysis of which leads to a species identified spectroscopically as the *N*-co-ordinated hydrogen cyanide complex  $[\text{Ru}(\text{NH}_3)_5(\text{HCN})]^{2+}$  are reported.

RECENT reports<sup>1-3</sup> have discussed the possible ligand properties of the cyanotrihydroborate ion,  $\text{BH}_3\text{CN}^-$ . In the present work, this ion, isoelectronic with acetonitrile, was used to synthesise the cationic complexes  $[\text{Ru}(\text{NH}_3)_5(\text{BH}_3\text{CN})]^+$  and  $[\text{Ru}(\text{NH}_3)_5(\text{BH}_3\text{CN})]^{2+}$ , both moderately stable in aqueous solution. The co-ordinated cyanotrihydroborate of each hydrolyses in acidic solution releasing hydrogen and leading, in the case of the former ion, to an isolable ruthenium(II)-hydrogen cyanide complex.

The reaction under argon between  $\text{NaBH}_3\text{CN}$  and  $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$  {prepared by  $\text{Zn}(\text{Hg})$  reduction of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}][\text{CF}_3\text{CO}_2]_2$  in neutral aqueous solution} gives a yellow-green solution. Sodium bromide causes precipitation of a yellow-green solid (I) which analyses (C,H,N) correctly for  $[\text{Ru}(\text{NH}_3)_5(\text{BH}_3\text{CN})]\text{Br}$  and has an i.r. spectrum analogous to that of the penta-ammineruthenium(II) complex of acetonitrile<sup>4</sup> (Table). When an aqueous solution of (I) is exposed to air for *ca.* 1 h, subsequent addition of  $\text{Br}^-$  precipitates a compound (II) which displays an i.r. spectrum analogous to that<sup>4</sup> of penta-ammine-(acetonitrile)ruthenium(III) (Table).

The similarity of certain ligand properties of  $\text{CH}_3\text{CN}$  and  $\text{BH}_3\text{CN}^-$  is illustrated by the  $\nu(\text{CN})$  increases for the  $\text{Ru}^{\text{III}}$  derivatives and the  $\nu(\text{CN})$  decreases for the corresponding  $\text{Ru}^{\text{II}}$  derivatives. Increased nitrile stretching frequencies are typical for  $\text{M}-\text{N}\equiv\text{C}-\text{R}$  type co-ordination to most metal

ions,<sup>5</sup> including Ru<sup>III</sup>,<sup>4</sup> and parallel the observations for the BH<sub>3</sub>CN<sup>-</sup> complexes of Cu<sup>I</sup>, Ag<sup>I</sup>, and Ni<sup>II</sup>.<sup>3</sup> The  $\nu(\text{CN})$  decreases on co-ordination of either BH<sub>3</sub>CN<sup>-</sup> or CH<sub>3</sub>CN to

frequencies expected for Ru<sup>II</sup> (Table) and does not display the BH<sub>3</sub> frequencies (*ca.* 2340 cm<sup>-1</sup>) observed for (I) and (II). In aqueous solution, (III) was stable only at very low

Complex	I.r. spectral data (cm <sup>-1</sup> ) <sup>a</sup>		
	$\nu(\text{CN})$	$\delta(\text{NH}_3)_{\text{sym}}$	$\rho(\text{NH}_3)$
NaBH <sub>3</sub> CN .. .. .	2180s		
[Ru(NH <sub>3</sub> ) <sub>5</sub> (BH <sub>3</sub> CN)]Br .. .. .	2170s	1253s	745s,br
[Ru(NH <sub>3</sub> ) <sub>5</sub> (BH <sub>3</sub> CN)]Br <sub>2</sub> .. .. .	2206s	1315s	805s,br
CH <sub>3</sub> CN .. .. .	2254s <sup>b</sup>		
[Ru(NH <sub>3</sub> ) <sub>5</sub> (CH <sub>3</sub> CN)] [BF <sub>4</sub> ] <sub>2</sub> .. .. .	2239s <sup>b</sup>	1258s <sup>c</sup>	773s,br <sup>c</sup>
[Ru(NH <sub>3</sub> ) <sub>5</sub> (CH <sub>3</sub> CN)] [ClO <sub>4</sub> ] <sub>3</sub> .. .. .	2286m <sup>b</sup>	1312s <sup>c</sup>	821s,br <sup>c</sup>
HCN(gas) .. .. .	2097s <sup>d</sup>		
[Ru(NH <sub>3</sub> ) <sub>5</sub> (HCN)] [ClO <sub>4</sub> ] <sub>2</sub> .. .. .	1960vs,br	1268s	765s,br

<sup>a</sup> All spectra taken on Perkin-Elmer 225 spectrometer, in KBr disc, except where noted.

<sup>b</sup> Ref. 4.

<sup>c</sup> R. E. Clarke and P. C. Ford, unpublished data.

<sup>d</sup> K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963, p. 80.

Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> are attributable to the  $\pi$ -backbonding noted for other Ru<sup>II</sup> organonitrile complexes.<sup>4,6</sup> The relatively low frequencies of  $\delta(\text{NH}_3)$  (symmetrical deformation) and  $\rho(\text{NH}_3)$  (rocking) for the Ru<sup>II</sup> ammines and the higher values for the Ru<sup>III</sup> ammines are characteristic of the ruthenium oxidation states.<sup>6</sup>

The u.v. spectra of the Ru<sup>II</sup> compounds are also similar, with  $\lambda_{\text{max}}$  224 nm ( $\log \epsilon$  4.1) for aqueous (I) compared with  $\lambda_{\text{max}}$  229 nm ( $\log \epsilon$  4.2)<sup>4</sup> for aqueous [Ru(NH<sub>3</sub>)<sub>5</sub>(CH<sub>3</sub>CN)]<sup>2+</sup>. The small shift of this absorption to shorter wavelength for (I) is consistent with the assignment of both bands as metal-to-ligand charge transfers (MLCT), as BH<sub>3</sub>CN<sup>-</sup> should be less electronegative than CH<sub>3</sub>CN.

Dissolution of [Ru(NH<sub>3</sub>)<sub>5</sub>(BH<sub>3</sub>CN)]Br in 3M-HCl leads to immediate formation of gas, presumably hydrogen, the product of borohydride hydrolysis. The u.v. spectrum of the product solution shows a new band at  $\lambda_{\text{max}}$  241 nm with an intensity ( $\log \epsilon$  *ca.* 4) comparable with that of the [Ru(NH<sub>3</sub>)<sub>5</sub>(BH<sub>3</sub>CN)]<sup>+</sup> MLCT band at 224 nm. Addition of sodium perchlorate precipitates (in high yield) a greenish-white solid (III), which displays an intense i.r. band (1960 cm<sup>-1</sup>) in the triple bond region and the  $\delta(\text{NH}_3)$  and  $\rho(\text{NH}_3)$

pH (*e.g.*, 3M-HCl), and decomposed immediately and irreversibly to unidentified products when the pH was raised, decomposing in minutes even at pH *ca.* 1. The same i.r. and u.v. spectra have been observed<sup>7</sup> for the product of the reaction between gaseous HCN and [Ru(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>2+</sup> in strongly acidic solution. A distinctly different species [*e.g.*,  $\nu(\text{CN})$  2010s,  $\delta(\text{NH}_3)_{\text{sym}}$  1265s, and  $\rho(\text{NH}_3)$  750 cm<sup>-1</sup>] is the product of the reaction between NaCN and [Ru(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>2+</sup> in neutral aqueous solution.<sup>7</sup>

The above i.r. data indicate that (III) is the hydrogen cyanide complex [Ru(NH<sub>3</sub>)<sub>5</sub>(HCN)] [ClO<sub>4</sub>]<sub>2</sub> co-ordinated at the nitrile nitrogen. In support, the u.v. band (241 nm) observed for (III) parallels MLCT bands observed for Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> co-ordinated CH<sub>3</sub>CN, BH<sub>3</sub>CN<sup>-</sup>, and N<sub>2</sub>,<sup>8</sup> a fact which suggests similar structural types. The pH sensitivity in aqueous solution indicates that *N*-co-ordinated cyanide ion (M-N≡C:) is an unfavourable configuration, and that the complex decomposes when the pH is high enough to generate this species.

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<sup>5</sup> R. A. Walton, *Quart. Rev.*, 1965, **19**, 126.

<sup>6</sup> P. C. Ford, *Coordination Chem. Rev.*, 1970, **5**, 75.

<sup>7</sup> R. E. Clarke, unpublished observations.

<sup>8</sup> I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Amer. Chem. Soc.*, 1969, **91**, 6512.