

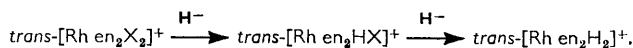
603. d-d Transitions in Hydrido-complexes. The Position of the Hydride Ion in the Spectrochemical Series.

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Spectroscopic data on a number of hydrido-complexes of rhodium(III) with nitrogen ligands are presented. The hydride ion is shown to fall in the spectrochemical series between water and ammonia.

It has been previously shown¹ that halide ions in ammine complex ions of rhodium(III) such as $[\text{Rh en}_2\text{Cl}_2]^+$ may be replaced by the hydride ion acting as a nucleophile. We have now been able to extend the previous studies substantially by measurements of the electronic spectra of ligand-field bands of the species involved in the substitution reactions in aqueous solutions at 0–2°, using a repetitive-scan spectrometer.

The reactions occurring when hydride ion (derived from borohydride in solution) attacks *trans*-dihalogenobisethylenediaminerhodium(III) cations, *trans*- $[\text{Rh en}_2\text{X}_2]^+$ (X = Cl, Br, I), are:



Several lines of evidence indicate that a two-stage reaction is occurring. The electronic spectra of aqueous solutions during the reactions show isosbestic points for both stages in all three cases (see Figs. 1 and 2). The disappearance of the original dihalogeno-complex

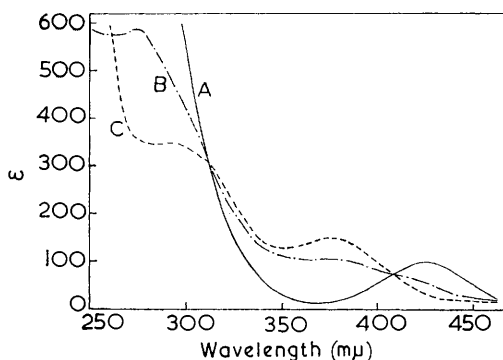


FIG. 1. Example of monohydride formation: $\text{trans-}[\text{Rh en}_2\text{Br}_2]^+ \longrightarrow \text{trans-}[\text{Rh en}_2\text{HBr}]^+$.

A, *trans*- $[\text{Rh en}_2\text{Br}_2]^+$; B, intermediate trace; C, *trans*- $[\text{Rh en}_2\text{HBr}]^+$.

Isosbestic points at 405 and 310 μ .

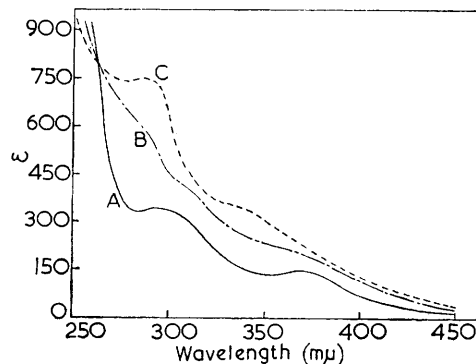


FIG. 2. Example of dihydride formation: $\text{trans-}[\text{Rh en}_2\text{HBr}]^+ \longrightarrow \text{trans-}[\text{Rh en}_2\text{H}_2]^+$.

A, *trans*- $[\text{Rh en}_2\text{HBr}]^+$; B, intermediate trace; C, *trans*- $[\text{Rh en}_2\text{H}_2]^+$.

Isosbestic point at 260 μ .

was accompanied by the growth of a new peak nearer the ultraviolet, whose position depended on which halide was originally present. On addition of more borohydride, this latter peak also decreased and a second peak even further into the ultraviolet appeared with increasing intensity. The position of the latter peak was independent of the original halogeno-complex used; its position and extinction coefficient were the same in all three cases. We formulate the intermediate species as the *trans*-hydridohalogenobisethylenediaminerhodium(III) complex, whilst the final product is the dihydro-complex ion. The assignment of *trans* stereochemistry to the intermediate monohydrido-species has been previously discussed.^{1b}

While electronic spectra proved the most sensitive means of studying the step-wise replacement reactions, attempts were made also to follow the growth and decay of the

¹ (a) Wilkinson, *Proc. Chem. Soc.*, 1961, 72; (b) Gillard and Wilkinson, *J.*, 1963, 3594.

intermediate monohydrido-species by use of proton magnetic resonance spectra. However, as a result of the transient nature of the intermediate and the comparatively low sensitivity of the n.m.r. method, we have been unable to observe the chemical shift of both the mono- and di-hydrido-species in the reduced solution from any *trans*-species, although both hydrides formed from *cis*-dichlorotriethylenetetraminerhodium(III) cation, discussed later, have been simultaneously observed.

We have been able to show, however, that the high-field line due to the dihydrido-species occurs at 1500 ± 10 c./sec. (relative to water), *i.e.*, $\tau \sim 31.6$ for the final products derived from all three original *trans*-dihalogeno-complexes. In all cases the resonance was split by 27 ± 1 c./sec. owing to the coupling with the ^{103}Rh nucleus. Only when *trans*-diiodobisethylenediaminerhodium(III) cation was treated with borohydride did the hydrido-halogeno-species attain a sufficiently high concentration for its high-field line to be observed (at 1420 ± 8 c./sec. relative to water, *i.e.*, $\tau \sim 30.2$). It was to be expected that the hydrido-iodo-species would be the intermediate species most likely to be detected by n.m.r., since its conversion into the dihydrido-species is more difficult to achieve than that of the other two halogeno-complexes, iodide being the poorest leaving group in nucleophilic substitution. The previous n.m.r. measurements¹ on the borohydride reduction of dichlorobisethylenediaminerhodium(III) cation at room temperature in the presence of excess of borohydride must be assigned to the final dihydrido-species.

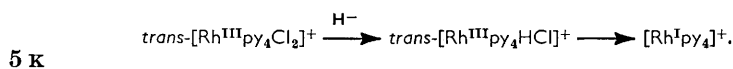
On addition of an aqueous solution of sodium tetraphenylborate to an ice-cold solution of *trans*-dihalogenobisethylenediaminerhodium(III) cations carefully treated with just less than the stoichiometric amount of borohydride required completely to form the halogenohydridobisethylenediaminerhodium(III) cation, tetraphenylborates were precipitated. These were evidently mixtures of the dihalogeno- and halogenohydrido-complexes. The infrared spectra show bands in the 2100 cm.^{-1} region which are assigned to the Rh-H stretching mode of the monohydrido-species. The position of the band varies slightly depending on the original halogeno-complex: 2100 cm.^{-1} in the chloro-, 2120 in the bromo-, and 2140 in the iodo-complexes. The previously reported¹ infrared absorption at 2100 cm.^{-1} observed in the tetraphenylborate precipitated from the ice-cold "reduced" solution of the *trans*-dichloro-complex is now seen to originate from the monohydrido-species. Whilst the tetraphenylborate of the dihydridobisethylenediaminerhodium(III) could be obtained as a white precipitate, it is exceedingly unstable, although it was previously shown^{1b} to contain no halogen.

Since this work on electronic spectra has now unequivocally located the position of the hydride ligand in the spectrochemical series, we have studied several analogous halogenoammine complexes of rhodium(III).

trans-Dichlorotetraminerhodium(III) chloride in ice-cold aqueous solution reacted extremely rapidly with a solution of borohydride, to form chlorohydridotetraminerhodium(III) cation, to which we assign *trans*-stereochemistry on the basis of the very close similarity of its electronic spectrum to that of the corresponding bisethylenediaminerhodium(III) complex. On addition of an excess of borohydride, the *trans*-chlorohydridotetraminerhodium(III) cation decomposed very rapidly, forming metallic rhodium.

A similar rapid nucleophilic replacement was observed when chloropentamminerhodium(III) cation was treated with hydride ion; the peak due to the lowest energy *d-d* transition in the chloropentammine species was seen to decay, and the growth of a new electronic spectral maximum was seen at $310 \text{ m}\mu$. This product, however, readily decomposed to metallic rhodium; the presence of finely dispersed rhodium probably accounts for the erroneous value of this new peak at $295 \text{ m}\mu$ previously reported.^{1b}

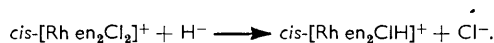
It was previously shown^{1b} that when *trans*-dichlorotetrapyridinerhodium(III) cation is treated with borohydride ion a hydrido-species is obtained giving a high-field line in the n.m.r. spectrum. The mechanism proposed was:



The hypsochromic shift of the longest-wavelength $d-d$ transition on a small addition of borohydride was compatible with the value expected for the formation of a *trans*-hydrido-chloro-species.

In the case of the analogous dibromo-complex, isosbestic points were observed for this first step. As expected for monohydrido-species, the lowest-energy transition was slightly lower in the species derived from the original dibromo-complex than in that derived from the dichloro-complex. On further addition of borohydride to either the hydridochloro- or hydridobromo-species, a new allowed band appeared in the near-ultraviolet, giving the solution a deep brown colour. This new band we tentatively attribute to the rhodium(I) species previously suggested.

In view of the observations supporting a two-stage substitution of chloride by hydride in the *trans*-dichlorobisethylenediaminerhodium(III) cation, we have re-examined the *cis*-isomer. The longest-wavelength transition in this compound is at $349\text{ m}\mu$, and spectral shifts on substitution by hydride ions are naturally not so marked; however, the band at $349\text{ m}\mu$ disappears, this process being characterised by an isosbestic point at $331\text{ m}\mu$ and the appearance of a shoulder at $340\text{ m}\mu$. We attribute this to the process:

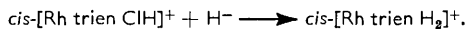


On further treatment with borohydride ion, the shoulder at $340\text{ m}\mu$ disappears, and the longest-wavelength band now at $295\text{ m}\mu$ has a broad tail to longer wavelength, and is rather strong ($\epsilon\ 1000$) for a $d-d$ transition. The final solution, which contains $cis-[Rh\ en_2H_2]^+$, shows a high-field line at 1525 c./sec. relative to water ($\tau\ \sim 32$). We have not been able to observe a high-field line for the monohydrido-species. Addition of a solution of sodium tetraphenylborate to the reduced solutions at appropriate stages yields precipitates of the hydrido-tetraphenylborate salts. The monohydride shows an absorption at 2105 cm.^{-1} in the infrared spectrum, and *cis*-dihydridobisethylenediaminerhodium(III) tetraphenylborate shows a strong band at 1969 cm.^{-1} . The latter salt, which contains no chlorine, rapidly reduces silver nitrate to silver. The *cis*-configuration is supported by the infrared spectrum in the NH_2 deformation region; absorptions occur at 1610 , 1577 , and 1560 cm.^{-1} . The occurrence of several absorptions in this region is characteristic² of the *cis*-bisethylenediaminerhodium(III) configuration.

cis-Dichlorotriethylenetetraminerhodium(III) cation behaves in an exactly similar way. On first adding sodium borohydride solution to the aqueous solution of the complex chloride, two isosbestic points are observed at 340 and $305\text{ m}\mu$, the band at $347\text{ m}\mu$ ($\epsilon\ 250$) due to the *cis*-dichloro-species begins to disappear, and a new band grows at $331\text{ m}\mu$ ($\epsilon\ 290$). The reaction occurring is:



cis-Chlorohydridotriethylenetetraminerhodium(III) tetraphenylborate shows an infrared absorption at 2081 cm.^{-1} . On addition of an excess of borohydride, the electronic spectrum again changes, the band at $331\text{ m}\mu$ in the monohydrido-species being replaced by a stronger band at $320\text{ m}\mu$ ($\epsilon\ \sim 400$). The second process is then:



cis-Dihydridotriethylenetetraminerhodium(III) tetraphenylborate, obtained from the solution of the second reduced species, shows absorption at 1969 cm.^{-1} . During the successive replacements of chloride ion by hydride ion, a high-field line ($\tau\ 28$) first appeared, due to the monohydride, which subsequently faded, while, at the same time, a second high-field line ($\tau\ 32.5$) (due to the dihydride) grew up. This was the only case where we observed the growth of the signal due to the dihydrido-species at the expense of the signal for the monohydride.

² Johnson and Basolo, *Inorg. Chem.*, 1962, **1**, 925.

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Spectroscopic data for the above complexes are collected in Table 1.

TABLE 1.
Spectra of rhodium complexes.

(Electronic spectra in $\mu\mu$, infrared spectra in cm^{-1} , n.m.r. spectra in τ values.)

[RhA ₄ X ₂] ⁺			[RhA ₄ XH] ⁺					
Formula	λ_{max}	*	λ	ϵ	λ	ϵ	τ	ν (Rh-H)
1 <i>trans</i> -[Rh en ₂ Cl ₂] ⁺ ...	406	388	365	85	—	—	—	2100
2 <i>trans</i> -[Rh(NH ₃) ₄ Cl ₂] ⁺	410	—	365	75	—	—	—	—
3 <i>trans</i> -[Rh en ₂ Br ₂] ⁺ ...	425	405, 310	371	150	296	350	—	2120
4 <i>trans</i> -[Rh en ₂ I ₂] ⁺ ...	462	410	385	350	—	—	30.2	2140
5 <i>trans</i> -[Rh py ₄ Cl ₂] ⁺ ...	410	—	355	120	—	—	28.5 †	—
6 <i>trans</i> -[Rh py ₄ Br ₂] ⁺ ...	432	410, 353	365	160	—	—	28.5 †	1976
7 [Rh(NH ₃) ₆ Cl] ²⁺ ...	343	—	310	—	—	—	—	2080
8 <i>cis</i> -[Rh en ₂ Cl ₂] ⁺ ...	349	331	340	—	—	—	—	2105
9 <i>cis</i> -[Rh trien Cl ₂] ⁺ ...	347	340, 305	331	290	—	—	28.0	2081 ‡

[RhA ₄ H ₂] ⁺							
	†	λ	ϵ	λ	ϵ	τ	ν (Rh-H)
1	254	(340)	350	290	680	31.6	—
2	—	—	—	—	—	—	—
3	260	(340)	350	291	700	31.6	—
4	244	(340)	400	291	850	31.6	—
5	—	—	—	—	—	—	—
6	—	—	—	—	—	—	—
7	—	—	—	—	—	—	—
8	—	295	10 ³	—	—	32.0	1969
9	—	320	400	—	—	32.5	1969

* Isosbestic point(s) for the process $[\text{RhA}_4\text{X}_2]^+ + \text{H}^- \rightarrow [\text{RhA}_4\text{XH}] + \text{X}^-$. † Isosbestic point for the process $[\text{RhA}_4\text{XH}] + \text{H}^- \rightarrow [\text{RhA}_4\text{H}_2]^+ + \text{X}^-$. ‡ Data from ref 1b.

The Hydride Ion in the Spectrochemical Series.—The hydride ion has been shown³ to cause more rapid substitution in the position *trans* to itself than any other anionic ligand. It was, therefore, predicted, on the basis of the high polarisability required to explain this large *trans*-effect, that the hydride ion should show a large ligand-field strength. The previous assessment⁴ of the position of the hydride ion in the spectrochemical series utilised a hydrido-complex stabilised by strong π -bonding ligands; since the *d-d* transitions in this complex are partially obscured by intense bands due to the charge-transfer and/or other allowed transitions, curve analysis was necessary. It was suggested⁴ that the hydride ion had a very large ligand-field strength, comparable with that of cyanide. Our observations of the *d-d* transitions in these octahedral complexes of amines, where allowed transitions occur only at higher energy, show conclusively that the hydride ion occupies a much lower position in the spectrochemical series. The appropriate data for series of related complex ions are given in Table 2 for complexes with D_{4h} symmetry, Table 3

TABLE 2.
Electronic spectra of complexes with D_{4h} symmetry.

Compound	${}^1A_{2g}, {}^1E_g \leftarrow {}^1A_{1g}$			${}^1B_{2g}, {}^1E_g \leftarrow {}^1A_{1g}$			Ref.
	λ	ν	ϵ	λ	ν	ϵ	
<i>trans</i> -[Rh en ₂ I ₂] ⁺ ...	462	21,650	260	—	—	—	This work and 2
<i>trans</i> -[Rh en ₂ Br ₂] ⁺ ...	425	23,530	100	—	—	—	This work and 2
<i>trans</i> -[Rh en ₂ Cl ₂] ⁺ ...	406	24,630	75	286	34,970	130	This work and 2
<i>trans</i> -[Rh en ₂ (N ₃) ₂] ⁺ ...	375	26,670	780	—	—	—	2
<i>trans</i> -[Rh en ₂ H ₂] ⁺ ...	340	29,410	250	290	34,480	500	This work
<i>trans</i> -[Rh en ₂ (NO ₂) ₂] ⁺	300(sh)	33,330	590	—	—	—	2

³ Basolo, Chatt, Gray, Pearson, and Shaw, *J.*, 1961, 2207.

⁴ Chatt and Hayter, *J.*, 1961, 772.

TABLE 3.
Electronic spectra of complexes of the type $trans\text{-}[\text{Rh en}_2\text{XCl}]^+$.

Compound	${}^1A_{2g}, {}^1E_g \leftarrow {}^1A_{1g}$			${}^1B_{2g}, {}^1E_g \leftarrow {}^1A_{1g}$			Ref.
	λ	ν	ϵ	λ	ν	ϵ	
$trans\text{-}[\text{Rh en}_2\text{ICl}]^+$	440	22,730	154	—	—	—	a
$trans\text{-}[\text{Rh en}_2\text{BrCl}]^+$	413	24,210	98	—	—	—	a
$trans\text{-}[\text{Rh en}_2\text{Cl}_2]^+$	406	24,630	75	286	34,970	130	b, c
$trans\text{-}[\text{Rh en}_2(\text{H}_2\text{O})\text{Cl}]^{2+}$	382	26,180	~66	280	35,710	—	a
$trans\text{-}[\text{Rh en}_2\text{HCl}]^+$	365	27,400	84	—	—	—	b
$trans\text{-}[\text{Rh en}_2(\text{NCS})\text{Cl}]^+$	363	27,550	340	—	—	—	c
$trans\text{-}[\text{Rh en}_2(\text{NH}_3)\text{Cl}]^{2+}$	342	29,240	95	295	36,360	120	c
$trans\text{-}[\text{Rh en}_2(\text{NO}_2)\text{Cl}]^+$	310	32,360	310	—	—	—	c

a, Bounsall and Poë, personal communication. b, This work. c, Ref. 2.

TABLE 4.
Electronic spectra of complexes with C_{4v} symmetry.

Compound	${}^1A_{2g}, {}^1E_g \leftarrow {}^1A_{1g}$			Ref.
	λ	ν	ϵ	
$trans\text{-}[\text{Rh en}_2\text{BrI}]$...	455	21,980	260	a
$trans\text{-}[\text{Rh en}_2\text{ClI}]$	440	22,730	154	a
$trans\text{-}[\text{Rh en}_2\text{HI}]$	385	25,970	220	b
$trans\text{-}[\text{Rh en}_2\text{HBr}]$...	371	26,950	160	b
$trans\text{-}[\text{Rh en}_2\text{HCl}]$...	365	27,400	84	b

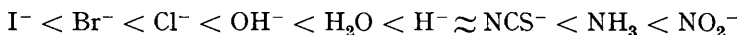
a, Bounsall and Poë, personal communication. b, This work.

TABLE 5.
Electronic spectra of $[\text{Rh}(\text{NH}_3)_5\text{X}]^+$ species.

Compound	${}^1E_g, {}^1A_{2g} \leftarrow {}^1A_{1g}$			Ref.
	λ	ν	ϵ	
$[\text{Rh}(\text{NH}_3)_5\text{I}]^{2+}$	388	25,800	230	a
$[\text{Rh}(\text{NH}_3)_5\text{Br}]^{2+}$	359	27,800	122	a
$[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$	349	28,700	100	a, b
$[\text{Rh}(\text{NH}_3)_5\text{OH}]^{2+}$	321	31,200	124	a
$[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	316	31,600	105	a
$[\text{Rh}(\text{NH}_3)_5\text{H}]^{2+}$	310	32,250	120	b
$[\text{Rh}(\text{NH}_3)_5]^{3+}$	306	32,700	135	a, b
$[\text{Rh}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$	296	33,800	330	a

a, Klixbull-Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 500. b, This work.

for complexes of the type $trans\text{-}[\text{Rh en}_2\text{XCl}]^+$, Table 4 for complexes with C_{4v} symmetry, and Table 5 for complexes of type $[\text{Rh}(\text{NH}_3)_5\text{X}]^{2+}$. All the results are consistent with the hydride ion's lying fairly low in the spectrochemical series between water and ammonia, *viz.*,



Metal-hydrogen bonds in complexes have sometimes been thought to be especially short. However, the present work shows that hydride ion behaves like a halide ion spectrochemically, giving transitions between states arising from the rhodium(III) ion, which is therefore not seriously perturbed by the hydride ion.

EXPERIMENTAL

Analyses were by the Microanalytical Laboratory, Imperial College. Infrared spectra were taken for mulls on a Grubb-Parsons Spectromaster instrument. Electronic spectra were taken with a Perkin-Elmer model 350 spectrophotometer with repetitive-scan accessory. Proton resonance spectra were taken at 56.43 Mc./sec. on a Varian V-4311 instrument.

For all samples prepared, infrared spectra of mulls and electronic spectra of aqueous solutions ($\sim 10^{-3}\text{M}$) were taken as a check on identification and purity.

All solvents were degassed. The nucleophilic replacements by borohydride were studied in 1-cm. silica cells maintained at 0–2° by circulating water from an ice-salt bath. Successive additions of ice-cold borohydride solutions were made by a syringe.

The borohydride solutions were made slightly alkaline (pH ~8) by addition of sodium hydroxide, which prevents much bubble formation which would have precluded accurate electronic spectral measurements. For our initial measurements, the cell compartments of the spectrophotometer were flushed by a rapid stream of dry nitrogen. However, this subsequently proved necessary only in the case of chloropentamminerhodium(III) chloride. Hydrido-species were isolated as their tetraphenylborate salts as previously described.¹⁰

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cis- and trans-Dihalogenobisethylenediaminerhodium(III) Salts and trans-Dichlorotetrammine-rhodium(III) Nitrate.—These were prepared by the method of Johnson and Basolo.² The infrared and electronic spectra of our samples agreed well with those published.

Chloropentamminerhodium(III) Chloride.—This was prepared by the method of Lebedinski.⁵

trans-Dichlorotetrapyridinerhodium(III) Chloride.—The preparation followed that of Gillard and Wilkinson.⁶

trans-Dibromotetrapyridinerhodium(III) Bromide.—The following is a more convenient preparation than those given in the literature. Rhodium(III) chloride trihydrate (1 g., 4×10^{-3} mole) in water (5 ml.) was added to a solution of potassium bromide (1.5 g., 1.5×10^{-2} mole) in water (5 ml.). Pyridine (2 ml.) was added and the mixture heated until just boiling. At this point, hypophosphorous acid (0.5 ml.) was carefully added dropwise, whereupon the solution turned yellow. On cooling, yellow-orange crystals of the salt appeared, which were recrystallised from water. Yield 1.8 g. (70%) (Found: C, 36.3; H, 3.15; N, 8.6. Calc. for $C_{20}H_{20}Br_3N_4Rh$: C, 36.5; H, 3.05; N, 8.5%). The infrared and electronic spectra agreed with those previously reported.⁷

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⁵ Lebedinski, *Ann. Inst. Platine*, 1936, **13**, 9.

⁶ Gillard and Wilkinson, *J.*, 1964, 1224.

⁷ Schmidtke, *Z. phys. Chem. (Frankfurt)*, 1962, **34**, 295.
