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The Preparation of Hydridopentammine- and Hydridoaquotetramminerhodium(III) Sulphates and Other Salts; the Formation of Alkyl and Fluoroalkyl Derivatives †

By K. Thomas, J. A. Osborn, A. R. Powell, and G. Wilkinson,* Inorganic Chemistry Research Laboratories, Imperial College, London S.W.7 and Research Laboratories, Johnson, Matthey, Ltd., Wembley, London

The action of metallic zinc on ammoniacal solutions of chloropentamminerhodium chloride in presence of sulphate ion leads to the formation of hydridopentamminerhodium(III) sulphate. Several other salts of the cation have been prepared.

The pentammine undergoes an aquation reaction to form the aquo-ion $[Rh(NH_s)_4(H_2O)H]^{2+}$ in which the water is trans to the hydrido-group.

The interaction of the hydrido-species with ethylene, propene, and but-l-ene and with tetrafluoroethylene and other fluoro-olefins has been studied and crystalline salts have been isolated. The i.r. and n.m.r. spectra of certain of these species are given, and the electronic spectra discussed.

THE preparation of cationic hydrido-complexes of rhodium(III) in which the complementary ligands were co-ordinated via nitrogen has been reported previously.¹ The preparation was by borohydride ion attack on aquous solutions of complexes such as $[RhCl_2 en_2]^+$; however, these complexes were isolated as the tetraphenylborate salts only and although the i.r. spectra of mulls clearly indicated the presence of a Rh-H bond, pure compounds were not obtained. The reaction liquors showed the high-field n.m.r. spectra characteristic for transition-metal hydrido-complexes and, despite relatively rapid decomposition, in some cases within an hour, the species were sufficiently stable to allow spectroscopic studies leading to the elucidation of the most probable reaction path for their formation and a suggested location for the hydride ion in the spectrochemical series.² The isolation of the sulphate salt of hydridopentamminerhodium(III) ion, [RhH(NH₃)₅]²⁺, previous evidence for which was only spectroscopic, has been reported briefly;³ this paper describes this complex and the related hydridoaquotetramminerhodium(III) ion and their reactions in greater detail.

Hydridopentamminerhodium(III) Sulphate.—The complex has been obtained as a white, microcrystalline solid by the action of zinc dust and ammonia upon an aqueous suspension of chloropentamminerhodium(III) chloride in the presence of ammonium sulphate. The sulphate salt is diamagnetic, appears to be stable indefinitely in dry air and shows both of the features characteristic for hydrogen bound to transition metals, namely a sharp, intense band in the i.r. at 2079 cm.⁻¹ and a highfield line in the n.m.r. spectrum which is a doublet, τ 27.1 [J (Rh-H) 14.5 c./sec.].

Other salts (Br⁻, I⁻, ClO_4^- , and $HgBr_4^{2-}$) of the hydridopentamminerhodium(III) cation have been prepared and their vibrational spectra measured for the range 4000-400 cm.⁻¹ (Table 1). Assignments for

 $\nu(\text{N-H})\text{, }\delta(\text{NH}_3)$ sym. and asym., $\rho(\text{NH}_3)\text{, and }\nu(\text{Rh-N})$ are clear on the basis of present knowledge,⁴ but we are unable to assign a medium strong band which occurs in the region of 1200 cm.⁻¹, varies in frequency with change in the anion and shifts on deuteriation $(v_{\rm H}/v_{\rm D})$ 1.3). This frequency is rather high compared with the usual region, 750–900 cm.⁻¹, for δ (M-H)⁵ although this is a possible assignment of the band. Deuteriation studies do not reveal any other band in the 750-900 cm.⁻¹ region which might be assigned as the Rh-H bending mode.

Of the ammine and hydride modes, all of which vary in frequency with variation in anion, $\nu(Rh-H)$ and $\nu(N-H)$ are the most sensitive decreasing in the order $ClO_4^- >$ SO₄²⁻ > I⁻ > [HgBr₄]²⁻ ~ Br⁻ ($\Delta\nu$ 111 cm.⁻¹) and ClO₄⁻ > SO₄²⁻ > [HgBr₄]²⁻ ~ Br⁻ ($\Delta\nu$ 100 cm.⁻¹) respectively. These trends are similar to those observed in a series of salts of the ion $[Co(NH_3)_6]^{3+}$, where hydrogen bonding between the co-ordinated ammine and the anion was proposed.⁶ The shift in Rh-H stretching frequency can also be explained on this basis with hydrogen bonding between the hydrido-ligand and the anion.

The sulphate salt is very soluble in water (ca. 160 g. 1.⁻¹). It is sufficiently stable so that even after 1 hr. at 40° in a concentrated ammonia solution in absence of air it can be recovered unchanged on cooling. The nature of the blue complex obtained on absorption of molecular oxygen ³ will be discussed separately.

Aqueous solutions decolourise permanganate and slightly acid solutions will reduce Cu2+ ion to copper (1 atom of Cu per Rh). With dilute sodium hydroxide. rhodium metal is deposited. On heating with very dilute hydrochloric acid, the solution turns brown slowly and precipitates approximately 60% of the rhodium as metal, whereas with more concentrated acid metal is not deposited. In both cases, mixtures of chloroammine complexes, so far unseparated, are obtained. On boiling with 50% acetic acid, approximately 50% of the rhodium

[†] No reprints available.

¹ (a) G. Wilkinson, Proc. Chem. Soc., 1961, 72; (b) R. D. Gillard and G. Wilkinson, J. Chem. Soc., 1963, 3594. ² J. A. Osborn, R. D. Gillard, and G. Wilkinson, J. Chem. Soc.,

^{1964, 3168.}

³ J. A. Osborn, A. R. Powell, and G. Wilkinson, Chem. Comm., 1966, 461.

W. P. Griffith, J. Chem. Soc. (A), 1966, 899.
 M. L. H. Green, Adv. Inorg. Chem. Radiochem., 1965, 7, 115.

⁶ J. Fujita, K. Nakamoto, and M. Kobayashi, J. Amer. Chem. Soc., 1956, 79, 3295.

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precipitates as metal, and from the green solution blue green crystals of $[Rh^{II}(OAc)_2(H_2O)]_2$ are obtained. The crystal structure of $[RhH(NH_3)_5](ClO_4)_2$ is being investigated.[†]

Hydridoaquotetramminerhodium(III) Sulphate.—The salt has been obtained as a chalk-white, air-stable solid from a dilute aqueous solution of hydridopent-amminerhodium(III) sulphate. The Rh-H stretching frequency is at 2146 cm.⁻¹ and shows a normal shift on deuteriation (ν_{Rh-H}/ν_{Rh-D} 1·39). It is not possible to assign $\rho(NH_3)$ unequivocally since two bands exist in the expected region. Both are of reduced intensity compared with $\rho(NH_3)$ for the salts of $[RhH(NH_3)_5]^{2+}$; however, it is possible that the sharper band at 828 cm.⁻¹

This lability of one ammonia group is attributable to the *trans*-weakening effect of the hydride and we thus assign *trans*-stereochemistry to the hydridoaquotetramminerhodium cation. In a related rhodium(III) species, only the aquo-ion $[RhH(CN)_4(H_2O)]^{2-}$ could be detected ⁷ and it may be noted that the addition of excess of NH₃ to this ion does not displace water, if we take the failure of the high-field line to shift as the criterion.

Insertion Reactions.—(a) Hydridopentamminerhodium(III) sulphate. Aqueous solutions of $[RhH(NH_3)_5]SO_4$ absorb ethylene, propene, but-1-ene, tetrafluoroethylene, hexafluoropropene, octafluorobut-2-ene, and hexafluorobut-2-yne, under mild conditions (1 atmos., 25°), to

	() 7 7 7 7		$\delta(\mathrm{NH}_3)$	$\delta(\mathrm{NH}_3)$						
Complex	$\nu(N-H)$	$\nu(Rn-H)$	asym.	sym.	$\rho(\mathbf{NH}_3)$	$\nu(Rh-N)$	Other bands			
[Rh(NH ₃) ₅ H]SO ₄	3293s 3152s	2079s	1629m	$1325 { m sh} \\ 1295 { m s} \\ 1250 { m w}$	859m 839m	465m 494w	1195s, 1082vs, 970w, 617s, 613s			
$[Rh(ND_3)_5D]SO_4$	2353s 2297s	1486s	116 3m	1002m	a	440w 472w	914m, 1082vs, 970w, 617s, 613s			
$[\mathrm{Rh}(\mathrm{NH}_3)_5\mathrm{H}](\mathrm{ClO}_4)_2\ldots\ldots$	3375s 3269s 3226sh	2126s	1623m	$\begin{array}{c} 1308 \mathrm{s} \\ 1282 \mathrm{sh} \end{array}$	789m	499w 479w 455w	1248m, 1081vs, 624vs, 560s			
$[\mathrm{Rh}(\mathrm{ND}_3)_5\mathrm{D}](\mathrm{ClO}_4)_2 \dots \dots$	2494s 2360s	1530m	1176 m	1005s	ь	432w 400w	960, 1081vs, 624vs			
$[Rh(NH_3)_5H]Br_2$	3276s 3186s	2015s	1609m	1278s	820s	483w 452m	1171m			
$[Rh(ND_3)_5D]Br_2$	2459s 2353s	۰ 1452	1059m	981m	616 m	448w 418w	912w, 901m			
$[\mathrm{Rh}(\mathrm{NH}_3)_5\mathrm{H}]\mathrm{I}_2$	3278s 3233s	2045s	1608s	1302m 1280s	806s	481w 452w	1181m			
$[Rh(NH_3)_5H][HgBr_4]$	3294s 3235s	2016s	1620s	1325m 1306s 1286m	795s	460w 457w	1221s, 1216s			
[Rh(NH ₃) ₅ Cl]Cl ₂	3258s 3177s		1553m	$\begin{array}{c} 1295 \mathrm{s} \\ 1263 \mathrm{w} \end{array}$	845s	518w 480w 470w				
$[Rh(NH_3)_5Cl]SO_4$	3212 s		1618m	1316s	883m	476w 449w	1087vs, 976w, 620s			
$[\mathrm{Rh}(\mathrm{NH}_3)_4(\mathrm{H}_2\mathrm{O})\mathrm{H}]\mathrm{SO}_4 \dots$	3160s 3300s	2146s	1638m	1320m 1290s 1252m	861m or 828 d	479w 463m 445w	1104vs, 1066vs, 973m, 816m, 619s, 610s, 569s (broad), 3480m,sh			

TABLE 1

I.r. spectra of hydridopentamminerhodium(III) salts (cm.⁻¹ in Nujol mulls)

^a Obscured by SO₄²⁻ bands. ^b Obscured by ClO₄⁻ bands. ^c Hexachlorobutadiene mull. ^d See discussion.

is due to the Rh-H bending mode which was not clearly assigned in the pentammine series.

The n.m.r. spectrum consists of a doublet, $\tau 32.0$, [J (Rh-H) 25 c./sec.]; this disappears on the addition of concentrated ammonia to be replaced by the doublet characteristic of [RhH(NH₃)₅]²⁺ and is regenerated immediately on acidification with concentrated sulphuric acid. These observations are consistent with the existence of an equilibrium

$$[RhH(NH_3)_5]^{2+} + H_2O \Longrightarrow [RhH(NH_3)_4(H_2O)]^{2+} + NH_3 (1)$$

From pH measurements of solutions containing various amounts of hydridopentammine sulphate (excluding CO_2), the known equilibrium constant for ammonia hydration, and neglecting any contribution from other ions, we can estimate the equilibrium constant for the aquation reaction (1) as $ca. 2 \times 10^{-4}$ at 25°.

form 1:1 complex cations in which the alkyl or perfluoroalkyl group is σ -bonded to rhodium, *e.g.*, with ethylene, $[RhEt(NH_3)_5]^{2+}$. All of the complex cations have been isolated as pure crystalline salts of one or more of the bromide, iodide, perchlorate, and sulphate anions. The rates of reaction decrease in the orders $C_2H_4 > C_3H_6 \sim C_4H_8$ and $C_4F_6 > C_2F_4 > C_3F_6 \sim C_4F_8$ and are inhibited by concentrated ammonia [in 3:2 v/v NH₃ ($d \ 0.880$)-H₂O, no absorption of ethylene occurred over 6 hr.]. Detailed analyses of the i.r. spectra are not attempted but the C-H and C-F stretching modes are clearly evident as peaks of medium and strong intensities respectively. The salt $[RhEt(NH_3)_5](ClO_4)_2$, after repeated treatment with D₂O, had an n.m.r. spectrum consisting of a triplet due to CH₃ protons centred

† By Professor J. A. Ibers.

⁷ D. N. Lawson, M. J. Mays, and G. Wilkinson, *J. Chem.* Soc. (A), 1966, 54.

at τ 9.2 [J (CH₂-CH₃) 7.6 c./sec.]. The methylene proton resonance signal appears as a shoulder on the high-field side of the ammine proton signal and consists of a double quartet centred at τ 7.6 [] (Rh-CH₂) 3.0 c./sec.]. The ammine signal persists even after repeated deuteriation but in low intensity. The ¹H n.m.r. spectrum of [Rh(C₂F₄H)(NH₃)₅]SO₄ in D₂O consists of a 1:2:1 triplet centred at τ 4.88 [$J(F_B-H)$ 56 c./sec.] with each peak further resolved into triplets $[J (F_{\alpha}-H)]$ 4.9 c./sec.; coupling due to rhodium was not detected. The ¹⁹F spectrum consists of two groups of lines centred at 73.3 (F_{α}) and 36.7 p.p.m. (F_{β}) below hexafluorobenzene as external reference. The group to low field consists of eleven lines in which a central multiplet of five lines (relative intensities 1:2:2:2:1) is flanked by 1:2:1 triplets. The central multiplet arises from two overlapping triplets; hence from first-order theory, we have the coupling constants J (Rh-F_a) 6, J (H-F_a) 4.9, and J (F_{α} - F_{β}) 1.2 c./sec. The high-field signal consists of a doublet only arising from J (H-F_{β}) 56 c./sec. The absence of F_{α} - F_{β} coupling in this signal is probably accounted for by a Rh- F_{β} coupling of approximately 0.5 c./sec. which results in broadening of the signal at half height with consequent lack of resolution. The low solubilities of the other insertion products precluded detailed analyses of their n.m.r. spectra.

It is interesting to note that the product formed with hexafluorobut-2-yne has an i.r. spectrum almost identical with that of the complex $(CO)_4MnC(CF_3)=C(CF_3)H.^8$ In particular the i.r. shows a band at 1596 cm.⁻¹ attributable to v(C=C) of a vinyl grouping, (cf. 1613 cm.⁻¹ in the manganese compound), suggesting the presence of only one stereoisomer.

(b) Hydridoaquotetramminerhodium(III) sulphate. Ethylene and tetrafluoroethylene are equally readily absorbed by aqueous solutions of $[RhH(NH_3)_4(H_2O)]SO_4$ to form complexes analogous to those of the hydridopentammine complex.

The n.m.r. spectrum of $[RhEt(NH_3)_4(H_2O)]SO_4$ in D_2O shows the same features as the pentammine analogue, the methyl proton signal consisting of a triplet centred at τ 9.2 $[J(CH_2-CH_3)$ 7.8 c./sec.] and the methylene proton signal consisting of a double quartet centred at τ 7.5 $[J(Rh-CH_2)$ 3.1 c./sec.].

The ¹H n.m.r. spectrum of the complex

[Rh(C₂F₄H)(NH₃)₄(H₂O)]SO₄ consists of the expected triple triplet centred at $\tau 4 \cdot 1$ [$J(F_{\beta}-H) 55$, $J(F_{\alpha}-H) 4 \cdot 0$ c./sec.]. The ¹⁹F spectrum consists of two groups of lines centred at 81.5 and 37.1 p.p.m. below hexafluorobenzene as external reference. The group to low field consists of an eleven-line multiplet which was resolved to give values of $J(Rh-F_{\alpha}) 6 \cdot 9$, $J(H-F_{\alpha}) 4$, and $J(F_{\beta}-F_{\alpha}) 5 \cdot 2$ c./sec. The signal to high field consists of a doublet, $J(H-F_{\beta}) 55$ c./sec., further split into triplets, $J(F_{\alpha}-F_{\beta}) 5 \cdot 2$ c./sec. (in contrast to the ¹⁹F spectrum of [Rh(C₂F₄H)(NH₃)₅]SO₄ where the high-field doublet was not further resolved).

⁸ P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, 1962, **3**, 511.

The lability of the *trans*-ammine ligand as discussed earlier is also evident in the alkyl and perfluoroalkyl series and is demonstrated by:

(i) $[RhEt(NH_3)_5](ClO_4)_2$ is isolated from solutions of $[RhEt(NH_3)_4(H_2\Omega)]SO_4$ after treatment with ammonia.

(ii) When one drop of concentrated ammonia is added to a solution of $[Rh(C_2F_4H)(NH_3)_4(H_2O)]SO_4$ contained in an n.m.r. tube, the ¹⁹F signal disappears instantaneously to be replaced by that characteristic of the pentammine complex. The process is reversed, only more slowly, when concentrated sulphuric acid is added, *i.e.*, the signal for $[Rh(C_2F_4H)(NH_3)_4(H_2O)]^{2+}$ is observed to grow whilst that for $[Rh(C_2F_4H)(NH_3)_5]^{2+}$ decays. Thus we have the aqueous equilibria

$$[RhEt(NN_3)_5]^{2+} + H_2O \xrightarrow[k_{-3}]{k_{-3}} [RhEt(NH_3)_4(H_2O)]^{2+} + NH_3 \quad (2)$$

and

$$[Rh(C_{2}F_{4}H)(NH_{3})_{5}]^{2+} + H_{2}O \xrightarrow[h_{-3}]{k_{2}}$$
$$[Rh(C_{2}F_{4}H)(NH_{3})_{4}(H_{2}O)]^{2+} + NH_{3} \quad (3)$$

Again, making the assumptions as above, we can estimate the values of K_2 as ca. 4×10^{-10} and K_3 as ca. 2×10^{-10} at 25°. K_2 and K_3 are several orders of magnitude less than K_1 ; even so it is noteworthy that the alkyl and perfluoroalkyl groups exert a considerably greater *trans*-labilising effect than does the chloride in [RhCl(NH₃)₅]²⁺.

(c) Reactions with mixed halogenofluoro-olefins. When solutions of [RhH(NH₃)₅]SO₄ are treated with CCl₂=CF₂, CBrF=CF₂, CF₃I, MeCl, and EtI, the corresponding halidopentamminerhodium(III) sulphate salt is formed as the exclusive solid product by halide-hydride exchange. This behaviour is to be contrasted with that of $HMn(CO)_5$ and $HCo(CO)_4$; e.g., with $HMn(CO)_5$, 1,1-dichloro-2,2-difluoroethylene yielded reduction and insertion products along with $Mn_2(CO)_{10}$ depending upon reaction conditions.⁹ The exchange reactions are much faster than 'insertion' reactions, *i.e.*, 1-2 hr. at normal temperatures, and since these reactions are essentially quantitative and only the sulphate salts rather than the halide salts are formed, the process presumably involves exchange via a four-centre transition state without halide ions existing free in solution.

Electronic Spectra and Discussion.—The electronic spectra of the complexes $[Rh(NH_3)_5X]^{2+}$, (X = H,alkyl, and perfluoroalkyl) measured in the range 400— 200 mµ are given in Table 2. The spectra show three bands; the high-intensity band to shorter wavelength can be attributed to a charge-transfer process and the two bands of low intensity (≈ 135 —330) at longer wavelengths can be assigned to the transitions $'E \leftarrow 'A_1$ and $'B_2 \leftarrow 'A_2$; of the latter two, the band to lower energy approximates to the value of the ligand-field

⁹ J. B. Wilford, A. Forster, and F. G. A. Stone, J. Chem. Soc., 1965, 6519.

Electronic spectra o	f rhodi	um com	plexes	
(λ, mµ;	v, cm.	-1)	-	
	L			
Complex	λ	v	ε	Ref.
$[Rh(NH_3)_5I]^{2+}$	388	25,800	230	a
[Rh(NH ₈) ₅ OH] ²⁺	321	31,200	124	a
$[Rh(NH_3)_5Et]^{2+}$	311	32,150	210	
$[Rh(NH_3)_5Pr]^{2+}$	311	32,150	225	
$[Rh(NH_3)_5Bu]^{2+}$	311	32,150	230	
$[Rh(NH_3)_5(NH_3)]^{2+}$	306	32,700	135	а
$[Rh(NH_s)_{t}H]^{2+}$	307 6	32,700		
$[Rh(NH_3)_5(NO_3)]^{2+}$	296	33,800	330	a
$[Rh(NH_3)_5C_2F_4H]^{2+}$	284	35,210	190	
$[Rh(NH_3)_5C_3F_5H]^{2+}$	284	35,210	270	
$[Rh(NH_3)_5C_4F_6H]^{2+}$	284	35,210	240	
$[Rh(NH_3)]_4(H_3O)Et]^{2+}$	310	32,250	170	
$[Rh(NH_3)]_4(H_3O)H]^{2+}$	300	33,350	280	
$[Rh(NH_3)_4(H_2O)C_2F_4H]^{2+}\dots$	288	34,700	230	
• C. K. Jørgensen, Acta	Chem.	Scand.,	1956, 10 ,	500.

^b Reflectance spectrum on ground solid.

splitting parameter Δ * and shows a hypsochromic shift order $I^- < Br^- < Cl^- < OH^- < H_0O <$ in the alkyl $< H^- \sim NH_3 < NO_2^- < perfluoroalkyl$. On this basis, the hydride and alkyl ligands occupy a fairly low position in the spectrochemical series while the fluoroalkyl groups are somewhat higher. Ligands have been classified ¹⁰ according to the atom co-ordinated to the metal ion, viz. I < Br < Cl < S < O < N < C. This classification is clearly an oversimplification since, in the case of carbon as the donor atom, the nature of the other atoms or groups on the ligand, e.g., Me and CF₂H, appreciably alters the ligand-field strength. However, applying this view to the spectra of the complexes [RhX(NH₃)₅]²⁺ assumes that all the rhodiumnitrogen bond lengths are the same, *i.e.*, each ammonia ligand has the same field strength. It is evident that the ammonia trans to the hydrido, alkyl, or perfluoroalkyl ligand is very labile, probably associated with a weak and long rhodium-nitrogen bond. Such bond lengthening has the effect of decreasing the contribution from the trans-ammonia; consequently, the ligand-field strength of the hydrido, alkyl, and fluoroalkyl ligands may be underestimated in such complexes. Indeed the apparent variation of the field strength of the hydridoligand from fairly low in complexes such as $[RhH(NH_3)_5]^{2+}$ to very high (see ref. 5) in $[CoH(CN)_5]^{3-}$ anion may result from such effects.

The greater stability of the pentammine perfluoroalkylrhodium complexes over the corresponding alkyl complexes as measured by the greater ligand-field stabilisation energy is ca. 9 kcal. mole⁻¹ and since this energy is (say) only 15% of the rhodium-carbon bond energy, it is somewhat surprising that more metal alkyls analogous to the many metal fluoroalkyls have not been prepared. It would appear that the reason is not necessarily thermodynamic in origin.

The reactions of $[RhH(NH_3)_5]^{2+}$ and

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 $[RhH(NH_3)_4(H_2O)]^{2+}$ cations with ethylene and other simple olefins is as yet one of the few examples of such 'insertion' reactions under mild conditions. The presence of a vacant or solvent-occupied site on the rhodium atom of RhCl₂H(PPh₃)₂,0.5CH₂Cl₂ in dichloromethane solution facilitates the formation of $RhCl_2Et(PPh_3)_2$ by initial attack of ethylene at the vacant site, followed by hydride transfer to the π bonded ethylene.¹¹ It is possible that such a criterion is a factor in the insertion reactions of olefins with $[RhH(NH_3)_5]^{2+}$ and $[RhH(NH_3)_4(H_2O)]^{2+}$ since a pentaco-ordinate species could arise via the scheme

$$[RhH(NH_{3})_{5}]^{2+} \rightleftharpoons [RhH(NH_{3})_{4}]^{2+} \rightleftharpoons [RhH(NH_{3})_{4}(H_{2}O)]^{2+}$$

Comprehensive kinetic data have not yet been obtained, however; a preliminary investigation of the rate of halide substitution indicates that the rate is dependent on the nature of the halide, *i.e.*, the rates decrease in the order $I^- > Br^- > Cl^-$, in contrast to substitution reactions in many octahedral complexes.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College, and A. Bernhardt, Mühlheim. I.r. spectra (in Nujol and hexachlorobutadiene mulls unless otherwise stated) were recorded on a Grubb-Parsons grating ' Spectromaster,' n.m.r. spectra on a Varian Associates 43100 at 56.5 Mc./sec., and electronic spectra on a Perkin-Elmer 350 instrument. All preparations were normally carried under nitrogen. Analyses are collected in Table 3.

Hydridopentamminerhodium(III) Sulphate.—To a solution of $[RhCl(NH_3)_5]Cl_2$ (6 g.), $(NH_4)_2SO_4$ (9 g.), and aqueous ammonia ($d \ 0.88$) (15 ml.) in water (30 ml.) held at 60° was added zinc dust (3 g.) in three aliquots over ca. 2 min. The mixture was held at $ca. 60^{\circ}$ for a further 2 min. after which time the pale yellow colour of the chloropentammine had disappeared. Undissolved zinc and a little rhodium metal were removed by filtration through a sintered filter and the colourless solution was cooled in ice. On saturation of this solution with ammonia gas the white complex was precipitated. The salt was contaminated with a second species, as yet unidentified but which has no i.r. absorption in the 2000 cm.⁻¹ region. It was readily removed by treating the crude product with degassed water (30 ml.) when a grey flocculate was formed; after filtration and resaturation of the ice-cold solution with ammonia the hydrido-complex was obtained. Repetition (2-3 times) of this procedure gave a white microcrystalline solid which was washed with acetone (20 ml.) and dried in vacuum at 20°. Yield 70–80% based on $[RhCl(NH_3)_5]Cl_2.$

Hydridopentamminerhodium(III) Perchlorate.—To a warm solution of [RhH(NH₃)₅]SO₄ (0.1 g.) in water (3 ml.) containing NH₃ solution (d 0.88) (0.1 ml.) was added saturated NaClO₄ solution (3 ml.). After ca. 2 min. white needles of the salt were formed which were collected, washed with water (10 ml.) and acetone (5 ml.), and dried in vacuum (12 hr.) (60%).

¹⁰ C. K. Jørgensen, 'Absorption Spectra and Chemical Bond-ing in Complexes,' Pergamon Press, London, 1962, p. 109.
¹¹ M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson,

J. Chem. Soc. (A), 1967, 1347.

^{*} Since the transition $A_2 \leftarrow A_1$ (which strictly should be observable under $C_{4\nu}$ symmetry) cannot be resolved from $E \leftarrow A_1$, the value of the latter transition can be said to approximate to Δ.

Hydridopentamminerhodium(III) Bromide.-

 $[RhH(NH_3)_5]SO_4$ (0.2 g.) was dissolved in the minimum of de-oxygenated water and the solution cooled to 5° under nitrogen. On addition of a saturated solution (5°) of KBr dropwise, the very pale yellow *bromide salt* was instantaneously precipitated. The collected solid was washed with air-free water (2 ml.) and acetone (5 ml.) and dried in vacuum at 20°. Yield, essentially quantitative.

Hydridopentamminerhodium(III) Iodide.—As for the bromide but using KI solution to give a rather deeper pale yellow salt.

Hydridopentamminerhodium(III) Tetrabromomercurate(II). —To a cold solution of $[RhH(NH_3)_5]SO_4$ (0.2 g.) in water (5 ml.) was added concentrated aqueous K₂HgBr₄ solution (prepared by mixing stoicheiometric amounts of KBr and quantitatively absorbed during 16 hr. Addition of warm NaClO₄ solution (10 ml. containing *ca.* 1 g.) gave white crystals of the *salt* which were washed with water (5 ml.) before drying *in vacuo* (50%). I.r. 3330s, 3275s, 3225s, 1620s, 1305s, 790s, 470w, 460w, and 445w (NH₃ ligands); 2955w, 2910m, 2880m, and 2835w (C-H stretch); others: 2050w, 2025w, 1365w, 1205s, 1090vs, 970w, 940m, 735m, 719m, and 625s, cm.⁻¹.

(b) Ethylpentamminerhodium(III) bromide. As above to yield on addition of KBr (10 ml., 1 g.) the salt as pale yellow crystals (35%). I.r. 3290s, 3172s, 1615s, 1290ms, 809s, 480w, and 456w (NH₃ ligands); 2827m, 2850m, 2896m, 2909m, and 2956m (C-H stretch); 1202m cm.⁻¹.

(c) Ethylpentamminerhodium(III) iodide. As above the salt was obtained on addition of KI (10 ml., 1 g.) as pale

					and the second	,								
		Analy	tical da	ata for	rhodi	um(111)) comp	lexes						
	Found (%)						Required (%)							
Complex	C	н	F	N	0	s	Xa	C	Н	F	N	0	S	X •
$[Rh(NH_a)_5H]SO_4$		5.5		$24 \cdot 4$	$22 \cdot 6$	11.0			$5 \cdot 6$		24.6	$22 \cdot 5$	11.2	
$[Rh(NH_3)_5H][ClO_4]_2$		4.1		17.8			18.1		4.1		18 ·0			18.3
[Rh(NH ₃) ₅ H]Br,		$4 \cdot 5$		19.8			$45 \cdot 8$		4.6		20.0			45.8
[Rh(NH,),H]I,		3.6		15.7			57.9		3.6		15.8			57.3
Rh(NH.).HITHgBr.				10.0			45.5				9.9			$45 \cdot 1$
Rh(NH,),(H,O)H)SO.		5.3		19.5	27.9	11-1			5.3		19.9	28.0	11.3	
Rh(NH), Et][ClO.]	6.1	4.7		16.8			17.7	5.8	4.8		16.8			17.1
$[Rh(NH_{a})]$ Et]Br.	6.6	5.3		18.7			-••	6.4	5.3		18.6			
[Rh(NH _a), Et]].	5.5	4.3		14.9			53.9	5.1	4.2		14.8			53.9
$[Rh(NH_{a}), (H_{a}O)Ft]SO.$	7.4	5.6		18.0	25.5	10.3		7.6	6.1		17.8	25.5	10.2	
$[Rh(NH_{*}), Pr][ClO_{*}]$	7.9	4.8		16.9				8.4	5.1		16.3			
$[Rh(NH_{2}), Bu][ClO_{4}]_{2}$	11.0	5.3		16.0				10.8	5.4		16.0			
$[Rh(NH_{*})_{*}(C,F,H)]SO.$	6.2	00	19.5	18.5		8.7		6.2	01	19.7	18.2		8.3	
[Rh(NH)] (C F H)][C][O]]	6.6		20.4	13.3		0.	13.0	6.7		91.9	13.0		00	13.0
[Rb(NH)] C F HISO	10.2		21.2	13.0		6.6	10 0	<u>0.0</u>		21.2	14.4		6.6	10 0
$(Rh(NH)) \cap F H)SO$	10.6		95.3	15.4		00		10.7		25.5	15.7		0.0	
$[Rh(NH_{1})/H \cap]C = HISO$	6.1	4.1	10.4	14.7		8.9		6.9		10.7	14.8		8.2	
1	01	. I. I.	10 1	14.1		- 52		04		10.1	1.1.0		00	

TABLE 3

^a Cl. Br. or I.

HgBr₂). The white precipitate of the salt obtained immediately was washed with water (1 ml.) and acetone (5 ml.) and dried in vacuum. Yield, essentially quantitative. Hydridoaquotetramminerhodium(111) Sulphate.—

 $[RhH(NH_3)_5]SO_4$ (2 g.) was dissolved in degassed water (50 ml.) at 30° and, after shaking under nitrogen for a few minutes, deoxygenated acetone (50 ml.) was added. The resulting suspension was agitated slowly for *ca.* 2 min. to coagulate the solid *complex* which was then collected on a sintered filter. The solid was washed with acetone (10 ml.) and redissolved in water (50 ml.) and the precipitation was repeated. Three cycles were adequate and the final pure salt was dried in vacuum at 20° (*ca.* 50%).

Interaction of Hydridopentamminerhodium(III) Sulphate with Olefins.—The solutions of $[RhH(NH_3)_5]SO_4$ were treated with the gaseous olefins in a closed system in which the gas taken up could be measured. Some preparations were also made for convenience in sealed glass pressure tubes. It is extremely important that the water used and the systems be free from oxygen; traces of oxygen appear to initiate decomposition of the solutions with the formation of rhodium metal. Once the complexes are formed, however, they are quite stable towards air and can be handled normally. All the following salts were recrystallised from water (below 60°) before analysis.

(a) Ethylpentamminerhodium(III) perchlorate. A solution of the hydridopentammine sulphate (0.5 g.) in water (10 ml.) was exposed to ethylene (1 atmos.); the gas was

yellow crystals (35%). I.r. 3260s, 3178s, 1615s, 1290s, 800m, 475w, and 450w (NH₃ ligands); 2950m, 2890m, 2885m, and 2820m (C-H stretch); 1202s cm.⁻¹.

(d) Propylpentamminerhodium(III) perchlorate. Using propene and [RhH(NH₃₎₅]SO₄ and procedure as in (a), the salt was obtained as white crystals (40%). I.r. 3355s, 3279s, 3223s, 1625s, 1300s, 793ms, 473w, and 460w (NH₃) ligands); 2955m, 2930m, 2895m, 2865m, and 2820w (C-H stretch); others: 2087w, 1456w, 1362w,sh., 1220ms, 1192ms, 1087vs, 934w, 699w, and 625s cm.⁻¹.

(e) Butylpentamminerhodium(III) perchlorate. As in (a) to give the salt as white crystals (35%). I.r. 3352s, 3280s, 3225s, 1620s, 1295s, 795s, 475w, and 455w (NH₃ ligands); 2970m, 2940m, 2925m, 2880m, 2865m, and 2820w (C-H stretch); others: 1460w, 1375w, 1232ms, 1193ms, 1180ms, 1087vs, 970w, 935w, 890w, 715w, and 625s cm.⁻¹.

Interaction of Hydridoaquotetramminerhodium(III) Sulphate with Ethylene.—As in (a) above except that, due to the lower solubility, $[RhH(NH_3)_4(H_2O)]SO_4$ (0.5 g.) in H_2O (50 ml.) was exposed to ethylene (1 atmos.); the takeup was again quantitative over 12 hr. The solution was then added to acetone (ca. 100 ml.) and stirred and the salt was collected, washed with acetone, and dried in vacuum (ca. 60%). I.r. 2920m, 2890m, 2852m, 2820w, and 2956m (C-H stretch); others: 3252s, 3155s, 1637s, 1465w, 1365s, 1321ms, 1292s, 1232w, 1200s, 1087vs, 1028m,sh, 975s, 840m, 826m, 625s, 615s, 607s, 490w, 465w, and 440w cm.⁻¹.

Interaction of Hydridopentamminerhodium(III) Sulphate

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with Fluoro-olefins.—In a thick-walled glass tube were placed $[RhH(NH_3)_5]SO_4$ (0.4 g.), water (5 ml.), and NH_3 solution (d 0.88) (0.2 ml.); after freezing and degassing, excess of fluoro-olefin (ca. 5 moles per mole Rh) was condensed in and the tube sealed. After shaking for ca. 2 days at 25°, the tubes were opened and the salts isolated as below.

Tetrafluoroethylene was prepared by the pyrolysis of polytetrafluoroethylene at $500-600^{\circ}$ and purified from perfluoropropene impurity by distillation at the temperature of a melting slush of light petroleum (b.p. $30-40^{\circ}$). The other fluoro-olefins were from the Peninsular Chemical Corporation.

(a) Tetrafluoroethylpentamminerhodium(III) sulphate. The ice-cooled solution was saturated with NH_3 gas to give white crystals of the salt which were washed with acetone (5 ml.) and dried in vacuum (ca. 80%). I.r. 3232s, 3077s, 1652m,sh, 1630m, 1341s, 1333s, 1298m, 1276m, 1150m,sh, 1138s,sh, 1086s, 1030s, 983m, 974m, 947s, 856m, 772m, 638m, 620s, 612s, 578m, 574m, and 539m cm.⁻¹.

(b) Hexafluoropropylpentamminerhodium(III) perchlorate. The reaction solution was filtered and a saturated solution of NaClO₄ added dropwise. The pale yellow crystals obtained were washed with acetone (5 ml.) and dried in vacuum (ca. 70%). I.r. 3343s, 3283s, 1622m, 1338s, 1271s, 1187s, 1155s, 1087s, 1000m, 965m, 845s, 794m, 721w, 689m, 666s, 595w, 558w, 533w, 574w, 471w, 459w, and 457w cm.⁻¹.

(c) Octafluorobutylpentamminerhodium(III) sulphate. The white crystals of the salt obtained by saturating the ice-

cooled solution with ammonia gas were washed with acetone (5 ml.) and dried *in vacuo* (60%). I.r. 3384s, 3171s, 1636s, 1345s, 1280s, 1261s, 1241s, 1192s, 1111s, 1001w, 971w, 954m, 917m, 896w, 865m, 821w, 807w, 783m, 768w, 717s, 684m, 677w, 671m, 668sh, 661m, 623s, 614s, and 446m cm.⁻¹.

(d) Hexafluorobut-2-enylpentamminerhodium(III) sulphate. The pale yellow crystals formed during reaction were collected, washed with acetone, and dried *in vacuo* (60%). I.r. 3406s, 3246s, 3185s, 1635m, 1596m, 1333s, 1298s, 1291s, 1277s, 1223m, 1159s, 1142s, 1105m, 1074s, 978m, 913m, 873m, 841m, 825m, 739m, 721m, 647s, 621s, 609s, 540w, 479w, and 445w cm.⁻¹.

Interaction of Hydridoaquotetramminerhodium(III) Sulphate with Tetrafluoroethylene.—[RhH(NH₃)₄H₂O]SO₄ (0·4 g.) was dissolved in degassed water (40 ml.) and stirred in an atmosphere of the olefin for 3 days at 25°. The solution was then added to acetone (80 ml.) and the precipitated white sulphate salt collected, washed with acetone, and dried in vacuum (ca. 60%). I.r. 3225vs, 3000m, 1605s, 1377ms, 1359w, 1335s, 1304s, 1245s, 1185m, 1087vs, 985s, 973s, 887m, 863s, 779w, 647s, 637s, 614s, 602s, 584s, 544w, 517w, 505w, 495w, 476w, and 437w cm.⁻¹.

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