

241. *Complexes of Rhodium(III) with Chlorine and Pyridine.*

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The reactions of chlororhodium(III) species with pyridine have been re-examined, and the nature of the products clarified. Spectral data are used to show that, in the pink polymeric substance formed in the separation of the isomers of trichlorotripyridinerhodium(III), the environment of the rhodium atoms is 2,3,4,5-tetrachloro-1,6-dipyridine.

COMPLEX compounds containing both chlorine and pyridine co-ordinated to rhodium(III) have been known for many years, the first, *trans*-dichlorotetrapyridinerhodium(III) chloride having been made by Jørgensen.¹ From our studies² on the reduction of such species it appeared that, despite the considerable amount of work on the preparation and properties of such complexes, there is a good deal of confusion in the literature.

The hexapyridinerhodium(III) cation is unknown, although Klixbull-Jørgensen has estimated³ that the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transition would occur at 30,000 cm.⁻¹. We have been unable to prepare either this or a pentapyridinerhodium(III) cation. The highest stable species is *trans*-dichlorotetrapyridinerhodium(III) cation, and we find that when treated with excess of pyridine (aqueous; anhydrous; refluxing; or in a sealed tube at 150°), this ion, as its chloride salt, slowly loses pyridine to form 1,2,6-trichlorotripyridinerhodium(III). In fact, under the most forcing conditions we used (the reaction of rhodium trichloride, or of the mixture of 1,2,3- and 1,2,6-trichlorotripyridinerhodium(III) or of *trans*-dichlorotetrapyridinerhodium(III) chloride, with excess of dry pyridine in a Carius tube at 150—180° for periods of up to 8 days) the only major product was 1,2,6-trichloropyridinerhodium(III). If hexapyridinerhodium(III) or pentapyridinerhodium(III) species were produced, the yield was certainly less than 1%. Experiments carried out in the presence of reducing agents such as ethanol or hypophosphorous acid were also unsuccessful. Neither did partial or complete removal of chloride give the desired products; dichlorotetrapyridinerhodium(III) nitrate was recovered unchanged after 12 hr. in refluxing excess of pyridine. After four days, a very small amount (*ca.* 1%) of 1,2,3-trichlorotripyridinerhodium(III) was isolated; it had presumably been formed by a disproportionation reaction, but no other product could be found. When dichlorotetrapyridinerhodium(III) chloride was treated with sufficient aqueous silver nitrate to remove all the ionic and co-ordinated chlorine (a very slow process even under reflux), and the resultant aqueous solution [presumably of *trans*-bisaquotetrapyridinerhodium(III) nitrate] refluxed with excess of pyridine, no change in the absorption spectrum could be observed during four days; dichlorotetrapyridinerhodium(III) chloride could be regenerated by treating the reaction mixture with hydrochloric acid. Chloropentamminerhodium(III) chloride can be recrystallized from boiling pyridine, which is not surprising in view of the observation,⁴ which we have confirmed, that ammonia displaces pyridine from dichlorotetrapyridinerhodium(III) chloride. The only claim to a hexapyridinerhodium species has been that for hexapyridinerhodium(II) chloride;⁵ as will be shown in a subsequent paper, this substance is, in fact, *trans*-dichlorotetrapyridinerhodium(III) chloride. Thus it seems likely that some kind of steric hindrance operates to prevent full hexaco-ordination of rhodium(III) by pyridine, and that the *cis*-dichlorotetrapyridinerhodium(III) cation is unknown for the same reason. Poulenc⁶ reported that heating a solution of *trans*-dichlorotetrapyridine(III)

¹ Jørgensen, *J. prakt. Chem.*, 1885, **27**, 478.

² Gillard and Wilkinson, *J.*, 1963, 3594.

³ Klixbull-Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 500.

⁴ Jørgensen, *J. prakt. Chem.*, 1889, **39**, 25.

⁵ Dwyer and Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1943, **76**, 275.

⁶ Poulenc, *Ann. Chim. France*, 1935, **4**, 632.

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chloride (*A*), in ethanol (which acts as a catalyst* in its preparation^{7a}) gave the 1,2,6-trichloro-isomer. We have confirmed this observation, and have also found that heating the solid hexahydrate of (*A*) *in vacuo* at 75° gives the anhydrous material, which subsequently loses pyridine on raising the temperature to 105°, again forming 1,2,6-trichlorotripyridinerhodium(III), (*B*). This non-electrolyte can be separated from the original salt, (*A*), by means of its solubility in chloroform or dichloromethane, with both of which it is known to form red solvates.

We were unable to confirm another reaction reported by Poulenc, *i.e.*, that a solution of *trans*-dichlorotetrapyridinerhodium(III) chloride, on exposure to sunlight, gives the 1,2,3-isomer of the trichloro-compound.

The reaction of rhodium trichloride with aqueous pyridine has been examined by several authors.⁷⁻⁹ The essential features, which we have confirmed, are, first, that the initial insoluble product is a mixture, (*X*), of 1,2,3- and 1,2,6-trichlorotripyridinerhodium(III) and, secondly, that the yellow filtrate from (*X*) gives crystals of (*A*); in one case, it was reported⁸ that, when these had been removed, refluxing the filtrate (which contained excess of pyridine) gave orange crystals, which were unidentified. We have also obtained these orange crystals, which are pure 1,2,6-trichlorotripyridinerhodium(III). This unexpected formation of the tripyridine species from the tetrapyridine species in excess of pyridine agrees with our other findings. It seems likely that the analytical⁸ value recorded for rhodium (25.4%) was rather high [(*B*) requires Rh, 23.04%]; high values obtained by weighing residues of combustion are, of course, common.

In both available descriptions^{8,9} of the attempted separation of isomers in (*X*), mention is made of a pink residue obtained on extraction of (*X*) with ethanolic chloroform; this residue was not characterized in one case,⁸ and formulated as $[\text{Rhpy}_2(\text{H}_2\text{O})(\text{OH})\text{Cl}_2]$ in the other,⁹ a band due to hydroxyl being observed in the infrared spectrum. We have obtained this rose-pink species from 1,2,6-trichlorotripyridinerhodium(III), (*B*), by several methods: (i) direct heating *in vacuo*; (ii) refluxing with chloroform; or (iii) merely exposing a solution of (*B*) in rigorously dried dichloromethane, in a closed container, to light for a few days. This third process was followed spectrophotometrically; the concentration of (*B*), measured by the peak at 425 m μ , had fallen to one half its original value after one week. It was clear from the successive spectra that the only rhodium-containing species present were the original trichloro-compound, (*B*), and the completely insoluble pink polymer; the absorption profile from 300 m μ to longer wavelengths was unchanged. The presence of free pyridine in the solution could be detected after a while by pumping off dichloromethane. It seems likely that this photochemical reaction is a charge-transfer process, associated with the well-known "pyridine" bands¹⁰ at around 280 m μ , which are most likely due to a delocalization of an electron from the (*t*_{2g})⁶ shell of the rhodium to a modified antibonding orbital of the pyridine. The pink polymer, previously reported^{8,9} as a preparative by-product, is, of course, an artefact of the method used (boiling with chloroform) for working up the mixture (*X*) of isomers of trichlorotripyridinerhodium(III).

The infrared and electronic (reflectance) spectra of all our pink products, (*P*), are identical; the absence of water or hydroxyl is shown by the infrared spectra, the formation in the absence of oxygen, and the analytical data, which indicate $[\text{Rhpy}_2\text{Cl}_3]$. A pink material may be formed by heating $[\text{Rhpy}_2\text{Cl}_3(\text{H}_2\text{O})]$, formed from *trans*-tetrachlorodipyridinerhodate(III) by aquation.^{7b} We find that this pink material has properties identical with those of (*P*), in particular that no absorption due to hydroxyl could be found in the

* The catalytic action of ethanol, and similar agents with active methylene groups, in rhodium substitution reactions is probably due to reduction to transitory rhodium(II) or hydrido-rhodium(III) species.

⁷ Delépine, (a) *Compt. rend.*, 1953, **236**, 559. (b) *Bull. Soc. chim. France*, 1929, **45**, 235.

⁸ Holtzclaw and Collman, *J. Amer. Chem. Soc.*, 1958, **80**, 2054.

⁹ Schmidtke, Cyanamid European Research Institute, Report TIC-P23, Geneva, 1962.

¹⁰ Klixbull-Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 151.

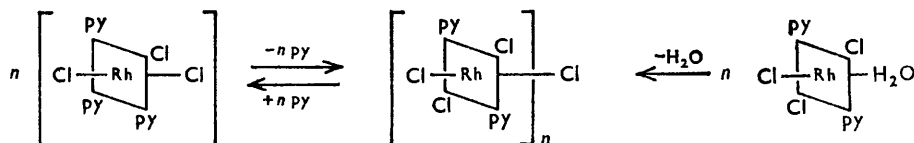
infrared spectrum. Analytical data for the pink species, which we formulate as $[\text{Rhpy}_2\text{Cl}_3]_n$, are given in Table 1.

TABLE 1.
Analytical data for the pink polymer.

Formula	Required						Found						Total
	C	H	Cl	N	O	Rh	C	H	Cl	N	O	Rh	
$[\text{Rh}_2\text{py}_4(\text{H}_2\text{O})\text{Cl}_6]^{2+}$ ^b	31.9	2.95	28.25	7.4	2.1	27.3	—	—	28.5	—	—	27.6 (28.3 ^b)	—
$[\text{Rhpy}_2(\text{H}_2\text{O})(\text{OH})\text{Cl}_2]^\ominus$ ⁹	32.7	3.5	19.3	7.6	8.7	28.0	34.0	3.1	19.5	7.65	4.9 ^c	28.5 (29.8 ^{c,9})	97.7
$[\text{Rhpy}_2\text{Cl}_3]_n^a$	32.7	2.7	28.9	7.6	—	28.0	32.9	3.0	28.5	7.1	abs.	28.1	99.7

^a This work; full analytical results are given in Experimental section. ^b Delépine pointed out that this analysis for the final product of heating, $[\text{Rhpy}_2\text{Cl}_3(\text{H}_2\text{O})]$, indicated Rhpy_2Cl_3 . ^c Based on combustion residue.

We therefore suggest the reaction-scheme shown below.



This accounts for the formula $[\text{Rhpy}_2\text{Cl}_3]_n$, the mode of formation from either 1,2,6-trichlorotripyridinerhodium(III), by loss of pyridine, or from 1,2,4-trichloro-3,5-dipyridine-6-aquorhodium(III), by loss of water, and the fact that prolonged refluxing of the pink polymer in pyridine gives a quantitative yield of 1,2,6-trichlorotripyridinerhodium(III). The environment of the rhodium(III) atoms in the pink polymer, assigned as 2,3,4,5-tetrachloro-1,6-dipyridine, is strongly indicated by the electronic spectrum (Table 2) which is strikingly similar to that of the *trans*-tetrachlorodipyridinerhodate(III) anion.

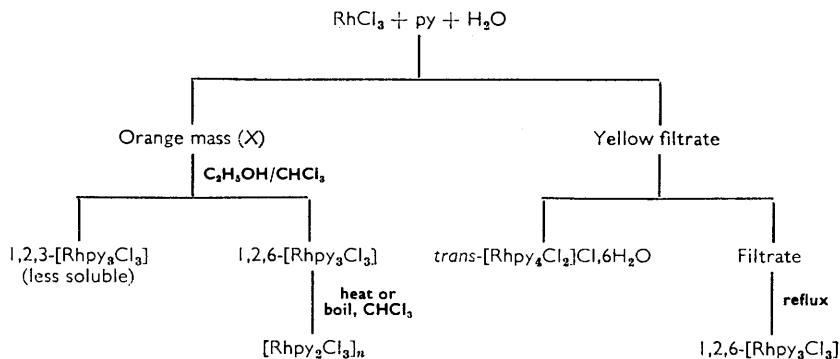
TABLE 2.

Electronic spectra of chloropyridinerhodium(III) complexes (λ in $m\mu$).

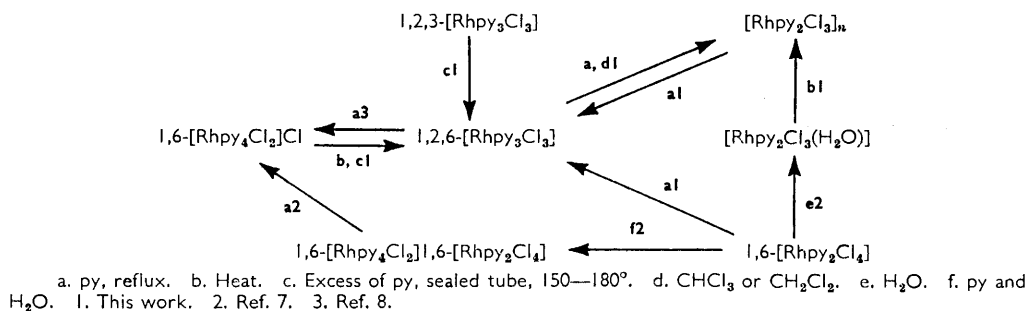
Complex	λ_1	ϵ_1	λ_2	ϵ_2	Conditions
<i>trans</i> - $[\text{Rhpy}_4\text{Cl}_2]^+$ ^a	411	80	305sh	200	ethanol
1,2,3- $[\text{Rhpy}_3\text{Cl}_3]^\ominus$ ⁹	407	140	—	—	—
1,2,6- $[\text{Rhpy}_3\text{Cl}_3]^b$	425	81	368sh	—	dichloromethane
"	438	—	—	—	reflectance
$[\text{Rhpy}_2\text{Cl}_3]_n$	518	^c	451	^c	reflectance
<i>trans</i> - $[\text{Rhpy}_2\text{Cl}_4]^-$	500	40	432	90	water
<i>cis</i> - $[\text{Rhpy}_2\text{Cl}_4]^{10}$	448	91	348	118	water

^a Ref. 10 gives: λ_1 411, ϵ_1 70. ^b Ref. 10 gives: λ_1 422, ϵ_1 76; ref. 9 gives: λ_1 428, ϵ_1 72. ^c ϵ_2 is certainly greater than ϵ_1 .

Schmidtke ⁹ formulated the pink compound obtained from treatment of a mixture of the isomers of trichloropyridine with chloroform (exactly the same conditions as give $[\text{Rhpy}_2\text{Cl}_3]_n$) as $[\text{Rhpy}_2(\text{H}_2\text{O})(\text{OH})\text{Cl}_2]$ and stated that it was soluble in dimethyl sulphoxide and was reprecipitated by water. We find, in fact, that a dispersion is formed in dimethyl sulphoxide which, on addition of water, deposits the pink material unchanged. If the dispersion is heated, a true solution is formed but only through disruption of the polymer. The solution is yellow and shows an electronic absorption spectrum (λ_{max} 430 $m\mu$) very similar to that of a solution of *trans*- $[\text{Rhpy}_2\text{Cl}_3(\text{H}_2\text{O})]$ in dimethyl sulphoxide (λ_{max} 420 $m\mu$), suggesting that a chlorine bridge has been broken by the polar solvent, giving presumably *trans*- $[\text{Rhpy}_2\text{Cl}_3(\text{OSMe}_2)]$; the longest wavelength absorption of *cis*- $[\text{Rhpy}_2\text{Cl}_3(\text{H}_2\text{O})]$ in dimethylsulphoxide is at 420 $m\mu$. We have no other evidence for other such chlorine-bridge cleavage reactions at present; triphenylphosphine, either molten or in ethanolic solution, does not affect the pink polymer.



The other "pink" by-product occasionally obtained⁹ in the preparation of chloropyridinerhodium(III) complexes, which is, in fact, distinctly yellow-pink, and which is insoluble in water but soluble in acetone and in chloroform, is the salt *trans*-dichlorotetrapyridinerhodium(III) *trans*-tetrachlorodipyridinerhodate(III), originally described by Delépine.^{7b} It has electronic absorption bands at 500, 432, and 411 m μ (ϵ 45, 90, and 102, respectively).



The reactions of rhodium trichloride with aqueous pyridine are summarized in Scheme 1 and the interconversions known within the series of pyridine complexes in Scheme 2. Infrared spectra are given in Table 3. The spectra of the trichloro-isomers were reported

TABLE 3.

Infrared spectra of chloropyridinerhodium(III) complexes (frequencies in cm.⁻¹).

1,2,3- [Rhpy ₃ Cl ₃]	1,2,6- [Rhpy ₃ Cl ₃]	1,6- [Rhpy ₄ Cl ₂]Cl*	[Rhpy ₂ Cl ₃] _n	1,2,3- [Rhpy ₃ Cl ₃]	1,2,6- [Rhpy ₃ Cl ₃]	1,6- [Rhpy ₄ Cl ₂]Cl*	[Rhpy ₂ Cl ₃] _n
1604s	1610m	1609s	1607m	1062s	1071 ^s	1062s	1067s
1481w	1485w	1485w	1486w	—	1067 ^s	—	—
1472w	1478w	1480sh	1479w	1009m	1016w	1014m	1017m
1446s	1450s	1450s	1449s	—	781m	—	—
—	1340w	—	—	760s	762s	764sh	—
1231w	1235m	1242w	1240w	752sh	754m	760s	758s
1205s	1212vs	1208s	1206s	—	699sh	—	—
1150w	1153m	1149s	1149m	692s	692s	689s	689s
—	1679sh	—	—	684w	686s	—	—

* The hexahydrate has extra bands at 3300vs,bd; 2700w,sp; 1641m,bd; 980w,bd; and 869w,bd cm.⁻¹.

in ref. 9, but those isomers were impure; their spectra are far more distinct than appeared. The weak band recorded⁸ at 720 cm.⁻¹ for rhodium trichloride (it was not specified whether this was anhydrous) is, we think, due to the use of Nujol as a mulling agent.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College. Infrared spectra, as Nujol mulls, were taken on a Perkin-Elmer model 21 spectrometer with calcium fluoride and sodium chloride optics. Electronic spectra in solution were measured by using a Perkin-Elmer model 350 spectrophotometer and reflectance spectra were obtained by use of the reflectance attachment to a Unicam S.P. 500 spectrophotometer.

Reaction of Rhodium Trichloride with Aqueous Pyridine.—The procedure of Holtzclaw and Collman⁸ was used. The first crop of crystals, (X), were collected, but the separation of the isomers was not satisfactory. Our subsequent work showed that the solid contained *ca.* 85% 1,2,6-trichlorotripyridinerhodium(III). The filtrate from (X) gave yellow crystals of *trans*-dichlorotetrapyridinerhodium(III) chloride hexahydrate which was recrystallised from water (Found: C, 38.1; H, 4.9; N, 8.9. Calc. for $C_{20}H_{32}Cl_2N_4O_6Rh$: C, 37.9; H, 5.1; N, 8.8%). An authentic sample of the tetrapyridine complex was obtained by a modification⁸ of Delépine's procedure.^{7a} The water of crystallization could be removed by pumping at 75°/1 mm. for 8 hr., when the loss of weight corresponded to 6H₂O.

By treating (X) (1.0 g.) with excess of pyridine (15 ml.) in a sealed tube at 150° for 3 days and allowing to cool, red-orange crystals of 1,2,6-trichlorotripyridinerhodium(III) were obtained (0.93 g., 93%) (Found: C, 40.2; H, 3.4; N, 9.5. Calc. for $C_{15}H_{15}Cl_3N_3Rh$: C, 40.3; H, 3.4; N, 9.4%). The compound was also recovered in very high yield (0.42 g., 93%) by treating anhydrous *trans*-dichlorotetrapyridinerhodium(III) chloride (0.53 g., 10⁻³ mole) with excess of pyridine (15 ml.) in a sealed tube at 160° for 4 days. Contrary to a previous report,⁸ 1,2,6-trichlorotripyridinerhodium(III) could be refluxed in ethanol for 2 hr. without any evidence of reduction to the metal.

Potassium *trans*-tetrachlorodipyridinerhodate(III) was prepared and aquated by the method of Delépine.^{7b} Pyridinium hexachlororhodate(III) was obtained as small red crystals by the method of Gutbier and Bertsch¹¹ (Found: C, 31.9; H, 3.4; N, 7.4. Calc. for $C_{15}H_{18}Cl_6N_3Rh$: C, 32.4; H, 3.3; N, 7.6%). The infrared spectrum showed absorptions (in cm.⁻¹) at: 3360s, bd; 2700m, bd; 1637m; 1606s; 1530s; 1240m; 1208s; 1192m; 1161m; 1147w; 1068s; 1049m; 768sh; 751s; 741sh; 694m; 680s.

Polymeric Trichlorodipyridinerhodium(III). Method 1. 1,2,6-Trichlorotripyridinerhodium(III) (0.45 g., 1 mmole) was kept *in vacuo* at 125° till it had become substantially pink (1 hr.). The product was allowed to cool and then extracted repeatedly with dichloromethane which removed the unchanged tripyridine complex. The rose-pink *complex* was collected and air-dried (0.27 g.) (Found: C, 32.9; H, 3.0; Cl, 28.5; N, 7.2; Rh, 28.1. $C_{10}H_{10}Cl_3N_2Rh$ requires C, 32.7; H, 2.7; Cl, 28.9; N, 7.6; Rh, 28.0%).

Method 2. A solution of 1,2,6-trichlorotripyridinerhodium(III) (0.23 g., 0.5 × mmole) in chloroform (35 ml.) was refluxed for 2 hr. and filtered while hot; the resulting pink solid (0.11 g.) was washed with hot chloroform (3 × 10 ml.) (Found: C, 32.3; H, 3.0; Cl, 28.6%).

Method 3. A solution of 1,2,6-trichlorotripyridinerhodium(III) (0.23 g.) in dichloromethane (15 ml.), previously dried by use of molecular sieves, was kept under nitrogen for 8 days. The pink solid which resulted (0.12 g.) was collected and washed with dichloromethane (Found: Cl, 28.6%).

Method 4. Orange 2,3,4-trichloro-1,6-dipyridine-5-aquorhodium(III) hydrate^{7b} (0.4 g.) was kept *in vacuo* at 115° until it had become substantially pink. After cooling, the solid residue was washed with hot water (in which the original compound is soluble) until no orange colour could be seen in the washings. The pink insoluble residue (0.32 g.) was washed with alcohol, then ether, and air dried (Found: C, 33.4; H, 2.9; Cl, 28.2%).

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¹¹ Gutbier and Bertsch, *Z. anorg. Chem.*, 1923, **129**, 67.