Syntheses and Properties of Some Oxalatorhodium(III) Complexes

By **A. W. Addison, R. D. Gillard,***† **P. S. Sheridan,** and **L. R. H. Tipping,** The Chemical Laboratory, University of Kent at Canterbury, Canterbury CT2 7NH

Replacements occur of halide (X) by oxalate ion ($C_2O_4^{2-}$,ox) in the complexes *trans*-$[RhL_4X_2]X$ [L = pyridine (py), 4-methylpyridine, and 3,5-lutidine] to give $[RhL_3X(ox)]$. A similar (but catalysed) formation from *trans*-$[Rh(en)_2Cl_2]Y$ of *cis*-$[Rh(en)_2L]Z$ (Y = NO_3^- or Cl^-; Z = ClO_4^-, NO_3^-, or $S_2O_6^{2-}$; en = ethylenediamine) has been achieved [L = oxalato(2−), malonato(2−), glycinato-*O*, or L-alaninato-*O*]. The utility of the oxalato-complexes in reactions (i) is illustrated for (*a*) L = L′ = ½en, X = Cl or Br, giving a convenient route into the *cis*-

$$[RhL_3L'(ox)]^{n+} + 2HX \longrightarrow [RhL_3L'X_2]^{n-} + H_2ox \qquad \text{(i)}$$

bis(ethylenediamine)rhodium(III) series, and (*b*) L = py, L′ = Cl, X = Br, or L = py, L′ = Br, X = Cl, giving novel mixed halogeno-complexes. Properties of the complexes $[RhL_3X(ox)]$ (L = py) are described, with vibrational spectra assigned through use of perdeuteriopyridine. The photosensitivity (originally noted by Poulenc in 1935) is shown to arise from reaction (ii). Some properties of the novel rhodium(I)-containing products of these

$$[Rh(py)_3(ox)X] \longrightarrow [Rh(py)_3X] + 2CO_2 \qquad \text{(ii)}$$

photoreductions are also described.

THE chemistry of rhodium has been widely studied, and emphasis in recent years has been on two major aspects. These are (*a*) complexes of π-bonding ligands such as phosphines with rhodium(I) and their catalytic properties in a range of contexts, and (*b*) complexes of σ-bonding ligands such as ethylenediamine with rhodium(III) and in particular mechanisms for catalytic substitution in rhodium(III) centres of this type.

Much effort has been devoted in this laboratory to work on complexes of pyridine and its analogues with rhodium(III); we have, for example, attributed the remarkable biological effects of complexes such as *trans*-$[Rh(py)_4X_2]Y$ (X = Cl or Br; Y = NO_3, Cl, or Br) to the ready formation of rhodium(I) species from them. It has become clear that a fuller understanding of the common ground between the areas (*a*) and (*b*) above [*i.e.* the reduced complexes of such mixed (σ + π) ligands as pyridine] would offer many clues in explaining the detailed chemistry of rhodium in aqueous media. We report here progress toward this end, in the form

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† *Present address:* Tatem Laboratories, University College, Cardiff CF1 1XL.

of some studies on complexes of the reducing ligand oxalate with rhodium(III), and a photochemical reduction of rhodium(III) to rhodium(I).

EXPERIMENTAL

Carbon, hydrogen, and nitrogen analyses, carried out using a Hewlett-Packard F.M. Scientific 185 C,H,N microanalyser, and halide analyses, carried out on a Radiometer PMT 1 phototitrator, were undertaken by Mr. G. Powell of this department. Analytical results are given in Table 1. Electronic spectra [given, with literature values, in Supplementary Publication No. SUP 20858 (5 pp.)] * were recorded using either Unicam SP 800 or Hitachi-Perkin-Elmer 124 spectrophotometers. I.r. spectra were measured for Nujol mulls between KBr plates, on a Perkin-Elmer 457 grating spectrophotometer. Far i.r. spectra of Polythene plates were measured on an R.I.I.C. Fourier-transform interferometer (FS-720), fitted with a FTS-100-7 computer (400—40 cm^{-1}).

TABLE 1

Analytical results (%)

Complex	C Found	C Calc.	H Found	H Calc.	N Found	N Calc.	Other Found	Other Calc.
mer-[Rh(py)$_3$Cl(ox)] (IV)	44·0	44·1	3·1	3·2	9·2	9·1		
mer-[Rh(py)$_3$Br(ox)] (V)	40·4	40·2	3·0	2·9	8·4	8·3		
mer-[Rh(γ-pic)$_3$Cl(ox)],4H_2O	41·9	41·6	5·0	5·1	7·4	7·3	11·8	12·5 (H_2O)
mer-[Rh(γ-pic)$_3$Cl(ox)] anhydrate	47·3	47·5	4·2	4·2				
mer-[Rh(lut)$_3$Cl(ox)]	50·2	50·4	5·0	4·9	7·6	7·7		
mer-[Rh(py)$_3$I(ox)]	36·1	36·8	2·2	2·7	7·8	7·6		
mer-[Rh(py)$_3$Cl$_3$]	40·2	40·3	3·4	3·4	9·2	9·4		
mer-[Rh(py)$_3$Br$_3$]	31·2	31·1	2·8	2·6	7·1	7·2		
mer-[Rh(py)$_3$ClBr$_2$]	33·7	33·7	2·9	2·8	8·1	7·9	6·8 30·8	6·6 (Cl) 29·9 (Br)
mer-[Rh(py)$_3$Cl$_2$Br]	36·5	36·7	3·1	3·1	8·6	8·6	14·7 16·5	14·4 (Cl) 16·3 (Br)
mer-[Rh({$^2H_5$}py)$_3$Cl$_3$]	39·2	39·1			9·2	9·1		
mer-[Rh(py)$_3$I$_3$]	24·9	25·0	2·3	2·1	5·9	5·8		
mer-[Rh(lut)$_3$Cl$_3$]	47·4	47·5	5·4	5·1	7·7	7·5		
[Rh(en)$_2$(ox)](ClO$_4$),$\frac{1}{2}H_2O$	17·2	17·1	4·3	4·3	13·4	13·3		
($C_6H_{17}ClN_4O_{8\cdot5}Rh$)	17·4	17·1	3·9	4·3	13·5	13·3	8·3	8·45 (Cl) [a]
[Rh(en)$_2$(mal)]NO$_3$ ($C_7H_{18}N_5O_7Rh$)	21·2	21·7	4·9	4·7	18·0	18·1		
[Rh(en)$_2$(gly)]S$_2$O$_6$ ($C_6H_2N_5O_8RhS_2$)	15·9	15·8	5·1	4·4	15·3	15·3		
[Rh(en)$_2$(ala)]S$_2$O$_6$ ($C_7H_{22}N_5O_8RhS_2$)	17·6	17·8	5·1	4·7	14·7	14·9		
[Rh(en)$_3$](ClO$_4$)$_3$,H_2O ($C_6H_{26}Cl_3N_6O_{13}Rh$)	11·9	12·0	4·1	4·3	14·2	14·0		
cis-[Rh(en)$_2$Cl$_2$]Cl,H_2O ($C_4H_{18}Cl_3N_4ORh$)	13·7	13·8	5·5	5·2	16·0	16·1		
trans-[Rh(en)(py)$_2$Cl$_2$]Cl,3H_2O ($C_{12}H_{24}Cl_3N_4O_3Rh$)	29·8	29·9	6·3	5·0	11·3	11·6		

[a] These analyses on a second sample of this complex were carried out as the result of a requirement by a referee.

Preparations.—*Rhodium*(III) *complexes with ethylenediamine* (*en*). Salts of complexes *trans*-[Rh(en)$_2$X$_2$]$^+$ (X = Cl, Br, NO$_2$, and N$_3$) were prepared and isolated as described by Johnson and Basolo.[1]

Bis(*ethylenediamine*)*oxalatorhodium*(III) *perchlorate*, [Rh(en)$_2$(ox)]ClO$_4$. An aqueous solution (25—30 cm^3) of the complex *trans*-[Rh(en)$_2$Cl$_2$]NO$_3$,H_2O (0·18 g, 0·05 mmol), $Na_2C_2O_4$ (0·10 g, 0·75 mmol), and NaOH (2 cm^3, 0·5M) was heated under reflux for *ca.* 1 min. A speck of $NaBH_4$ was added to the boiling solution, and refluxing was continued for 15 min. To the cooled, well filtered, solution, $LiClO_4$ (*ca.* 0·8 g in 15 cm^3 H_2O) was added, and the volume of the solution reduced to *ca.* 25 cm^3. The white precipitate which formed on cooling was collected by filtration, washed well with cold water, ethanol, and diethyl ether, and air-dried. Our convenient resolution of this complex into enantiomers will be given elsewhere.

Bis(*ethylenediamine*)*malonatorhodium*(III) *nitrate*, [Rh(en)$_2$(mal)]NO$_3$. An aqueous solution (25 cm^3) of the complex *trans*-[Rh(en)$_2$Cl$_2$]NO$_3$,H_2O (0·18 g, 0·5 mmol), malonic acid (0·5 g, 4·8 mmol), and NaOH (*ca.* 10 cm^3, 0·5M) was heated under reflux for *ca.* 1 min. A speck of $NaBH_4$ was added to the boiling solution, and refluxing was continued for an additional 50 min. Two drops of concentrated HNO_3 were added to the cooled solution, which was then reduced to *ca.* 3 cm^3. After carefully removing any traces of rhodium metal, the solution was kept for 10 days in a refrigerator. The rectangular crystals which formed were collected by filtration, washed with cold water, ethanol, and diethyl ether, and air-dried.

Bis(*ethylenediamine*)(*glycinato*-O)*rhodium*(III) *dithionate*, [Rh(en)$_2$(gly)]S$_2$O$_6$. An aqueous solution (25—30 cm^3) of the complex *trans*-[Rh(en)$_2$Cl$_2$]NO$_3$,H_2O (0·18 g, 0·5 mmol), glycine (0·45 g, 0·6 mmol), and NaOH (2 cm^3, 0·5M) was heated under reflux for *ca.* 1 min. A speck of $NaBH_4$ was added to the boiling solution, and refluxing was continued for 10 min. To the cooled, well filtered, solution $Na_2S_2O_6$ (*ca.* 0·5 g in 10 cm^3 H_2O) was added, and the volume of the solution reduced to *ca.* 15 cm^3. The white precipitate which formed on cooling was collected by filtration, washed with cold water, ethanol, and diethyl ether, and air-dried.

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* For details see Notice to Authors in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

[1] S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1962, **1**, 925.

(*Alaninato*-O)*bis*(*ethylenediamine*)*rhodium*(III) *dithionate*, [Rh(en)$_2$(ala)]S$_2$O$_6$. This complex was prepared in a manner analogous to the preparation of [Rh(en)$_2$(gly)]S$_2$O$_6$ described above, except that 0·053 g (0·6 mmol) of L-alanine was used instead of glycine. Although, in principle, two diastereoisomeric cations may be present, *i.e.* the D and L hands of the complex each containing the L-alaninate ligand, we have not studied possible stereoselective effects. Any stereoselectivity would be reduced by proton exchange (and consequent racemization) at the asymmetric carbon atom, but we have not yet evaluated the significance of this feature.

Tris(*ethylenediamine*)*rhodium*(III) *perchlorate*, [Rh(en)$_3$](ClO$_4$)$_3$. An aqueous solution (25 cm^3) of the complex *trans*-[Rh(en)$_2$Cl$_2$]NO$_3$,H$_2$O (0·18 g, 0·5 mmol) and ethylenediamine [1·8 cm^3 of a solution prepared by diluting neat ethylenediamine (1 cm^3) to 50 cm^3 with water, 0·5 mmol] was heated under reflux for *ca.* 1 min. A speck of NaBH$_4$ was added, and refluxing continued for another 5—10 min. To the cooled, well filtered, solution, LiClO$_4$ (*ca.* 0·5 g in 15 cm^3 H$_2$O) was added, and the volume of the solution reduced to 5—10 cm^3. After cooling in a refrigerator for several days, the white precipitate of the monohydrate which formed was collected by filtration, washed extensively with methylated spirits, then with diethyl ether, and air-dried.

cis-*Dichlorobis*(*ethylenediamine*)*rhodium*(III) *ion*, cis-[Rh(en)$_2$Cl$_2$]$^+$. Two methods were developed for the preparation of this complex.

(a) cis-[Rh(en)$_2$Cl$_2$]NO$_3$. The method [1] of Johnson and Basolo was used with three modifications: (*i*) Na$_3$[RhCl$_6$],12H$_2$O replaced RhCl$_3$,3H$_2$O as a source of rhodium; (*ii*) the total time of heating under reflux was reduced to *ca.* 5 min; and (*iii*) the solution was never allowed to become alkaline. An aqueous solution of Na$_3$[RhCl$_6$],12H$_2$O (1·72 g) and ethylenediamine dihydrochloride (1·01 g) was heated until reflux began. A solution of NaOH (*ca.* 2M) was steadily added (dropwise) to the refluxing solution until pH 7. Once neutral, the reaction mixture was removed from the heat source, and quickly acidified with HNO$_3$; products were isolated as described [1] by Johnson and Basolo. The first product was still *trans*-[Rh(en)$_2$Cl$_2$]NO$_3$,H$_2$O, but the filtrate gave *cis*-[Rh(en)$_2$Cl$_2$]NO$_3$ in higher yields than previously isolated (*ca.* 20% based on Rh).

(b) cis-[Rh(en)$_2$Cl$_2$]Cl. An aqueous solution (20 cm^3) of the complex [Rh(en)$_2$(ox)]ClO$_4$ (0·10 g, 0·25 mmol), acidified with 5 cm^3 concentrated HCl, was heated under reflux for *ca.* 3 min. The solution was cooled and reduced in volume to *ca.* 5 cm^3 and cooled over ice for several hours. The yellow precipitate which formed was collected by filtration, washed carefully with cold water, then methylated spirits, and air-dried. Yield 0·05 g *cis*-[Rh(en)$_2$Cl$_2$]Cl,H$_2$O, 64% based on Rh. Electronic and i.r. spectra agreed with published data. When HBr was used instead of HCl, an otherwise identical procedure yielded *cis*-[Rh(en)$_2$Br$_2$]Br.

trans-*Dichloro*(*ethylenediamine*)*dipyridinerhodium*(III) *chloride trihydrate*. The complex *trans*-[Rh(py)$_4$Cl$_2$]Cl,5H$_2$O (0·5 g) and ethylenediaminium monochloride (0·05 g) were heated under reflux overnight in aqueous ethanol (40 cm^3, 25% v/v). The resultant solution was concentrated to 10 cm^3 on a steam-bath, then allowed to cool, when orange-yellow rhombs (0·08 g) were obtained, which were washed with cold water and air-dried. Although Meyer and Kienitz [2] have prepared this salt by reaction (as a paste with neat ethylenediamine, heated on a steam-bath) of the complex *trans*-[Rh(py)$_4$Cl$_2$]Cl, their synthesis has not been reproduced.[3] The evidence for our formulation as given, involving the distinct monomeric cation *trans*-[Rh(en)(py)$_2$Cl$_2$], (I), rather than as a 1 : 1 lattice compound of *trans*-[Rh(en)$_2$Cl$_2$]Cl, (II), and *trans*-[Rh(py)$_4$Cl$_2$]Cl, (III), comes from (*i*) electronic spectra, given in SUP 20858, where, although the positions (and intensities approximately) of the pyridine π–π^* bands and of the second ligand-field band may be interpolated between those of complexes (II) and (III), the molar absorbance of the first ligand-field band of (II) is increased, well beyond experimental error, (*ii*) Raman spectra, where the absence of the unit *trans*-[Rh(py)$_4$Cl$_2$]$^+$ is supported by the absence of the strong bands which occur at 215 and 270 cm^{-1} in (III) [ν_{sym}(Rh–Cl) occurs as a very strong band at 305 cm^{-1}, and there is also a band of medium intensity at 356 cm^{-1}. The i.r. spectrum (400—4 000 cm^{-1}) contains the features of complexes (II) and (III), and is not useful in differentiating (II)], and (*iii*) *X*-ray powder photographs, data given in SUP 20858, which are quite dissimilar for complexes (I), (II), and (III).

Rhodium(III) *complexes with pyridine*. Halogeno-oxalatotripyridinerhodium(III) complexes were obtained by the original procedure,[4] or by catalysed reaction (tetrahydroborate) of a warm aqueous solution containing the *trans*-[Rh(py)$_4$X$_2$]X salt (0·5 g) and potassium oxalate (0·3 g; we used this because it dissolves more readily than the sodium salt). Yields were 95—100% of feathery yellow (X = Cl) or orange (X = Br) needles.

mer-*Chlorotris*(3,5-*dimethylpyridine*)*oxalatorhodium*(III) and other complexes with paraffinic substituents were best prepared by adding potassium oxalate (0·8 g) to the chloride salt of the complex (0·4 g) in boiling aqueous ethanol (10% v/v, *ca.* 60 cm^3). Boiling redissolved the cream flocculent initial precipitate (oxalate salt) (more ethanol was added if needed) and after 2—3 min caused evolution of heteroaromatic compounds (odour) and crystallization of the desired complex. The latter was removed from the solution on cooling and washed with warm water. Yield 0·3 g yellow platelets, soluble in alcohols and chloroform.

mer-*Trihalogenotripyridinerhodium*(III) complexes were obtained from the halogeno-oxalato-precursors, [Rh(py)$_3$X(ox)] (0·5 g), by dissolving them in hot hydrochloric or hydrobromic acid (HX, 25 cm^3) and allowing the solutions to stand overnight. The crystals (85—95% yields) were filtered off, washed with hot water, and recrystallized from chloroform by evaporation. The halogenocarbon solutions are photosensitive, and also give solvates which we describe elsewhere. Oxalato-complexes with substituted pyridine ligands (lutidine, lut) required methanolic hydrohalogenic acid for the reaction. The γ-picoline (γ-pic) complex in CHCl$_3$ solution had λ 425 nm (ε 78 l mol^{-1} cm^{-1}). ^{1}H N.m.r. resonances due to the two different methyl groups were coincident at 60 MHz but the 220 MHz spectrum showed two peaks at 7·59 and 7·57 in the expected ratio of 2 : 1.

The tri-iodo-complex, *mer*-[Rh(py)$_3$I$_3$], was obtained as plum-coloured crystals by boiling a solution of *trans*-[Rh(py)$_4$Cl$_2$]Cl in aqueous ethanol with an excess of iodide ion and a small amount of pyridine. Reaction of iodide

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[2] J. Meyer and H. Kienitz, *Z. anorg. Chem.*, 1939, **242**, 281.

[3] R. D. Gillard, E. D. McKenzie, and M. D. Ross, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1429.

[4] L. Tchugaev, *Bull. Soc. chim. France*, 1919, **25**, 234.

ion in acidic solution with the oxalato-complexes did not give readily purifiable products and was not pursued.

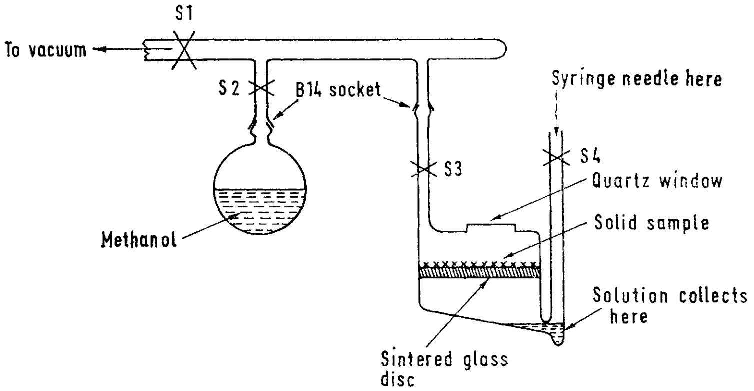
Irradiations.—Irradiations were undertaken on solid samples using a 150 W medium-pressure mercury lamp (periods of 3—4 days gave enough photoproduct). Gaseous products were analysed by i.r. and mass spectrometry, and the amount of gas produced was measured by manometry. Solid products were characterized using i.r., far i.r., electronic, and mass spectrometry.

Blank experiments. The conditions for the photochemical reactions discussed below (*e.g.*, with Cl_2) were reproduced in the dark. No dark reactions occurred. The thermal stability of the complex *mer*-[Rh(py)$_3$(ox)Cl] was also studied. The complex *mer*-[Rh(py)$_3$(ox)Cl] (7·25 mg) was heated under an atmosphere of argon using a Perkin-Elmer DSCI-B differential scanning calorimeter, from 290 to 700 K. At 525 K (252 °C) the complex decomposed (endothermic reaction). The final weight was 2·52 mg. White needles sublimed out above 600 K, leaving a black residue.

Irradiation of mer-[Rh(py)$_3$(ox)Cl] in vacuo. The complex *mer*-[Rh(py)$_3$(ox)Cl] (*ca.* 1·2 g) was irradiated using the apparatus shown in the Figure. A known weight of solid, on the sintered glass disc, was irradiated, the apparatus being shaken every few hours to renew the surface. When the entire surface of the solid had become brick red (*ca.* 4 days) the gas produced was condensed (cold-finger) and the manometric pressure measured. Degassed methanol was then added to the cell by condensing it *in vacuo* on to the solid sample. A yellow-black solution was produced whose n.m.r. spectrum was measured. The weight of the residual starting material after this removal of red photoproduct was recorded. In a typical experiment, 0·117 g (0·252 mmol) [Rh(py)$_3$(ox)Cl] was solubilized (*i.e.* had reacted) and gave 0·431 mmol CO_2. The i.r. spectrum of the gas had bands at 3 710 and 3 700 (weak doublet), 3 610 and 3 595 (weak doublet), and 2 310 cm^{-1} (v. broad and strong); the spectrum was identical to that of authentic CO_2. The mass spectrum showed only a strong *m*/*e* peak at 44.

Reactions of the photoproduct: (a) *with formaldehyde and triphenylphosphine*. No reaction took place between the complex *mer*-[Rh(py)$_3$(ox)Cl], Ph_3P, and HCHO in absolute ethanol even on heating the solution to boiling. The complex (*ca.* 0·5 g) was irradiated in a test tube *in vacuo* for 4 days. The resulting red solid was then dissolved in absolute ethanol *in vacuo* and triphenylphosphine in absolute ethanol was added followed by formaldehyde. The reaction mixture, which became yellow-brown, was heated to boiling and unreacted starting material removed. The hot filtrate was allowed to cool giving crystals whose i.r. spectrum (1 960s, 1 092s, 752s, 690s, 585s, 540sh, 527s, 512s, and 505s cm^{-1}) was identical to that of authentic [Rh(PPh$_3$)$_2$(CO)Cl] (1 960s, 1 092s, 754s, 690s, 585s, 540sh, 529s, 512s, and 505s cm^{-1}).

(b) *With dichlorine*. (i) The complex *mer*-[Rh(py)$_3$(ox)Cl] (*ca.* 0·15 g) was irradiated for 4 days *in vacuo*. The gas was pumped off and chlorine added to the red solid, which then became yellow. The product was separated from starting material by extracting it with chloroform; its far i.r. spectrum showed that it was *mer*-[Rh(py)$_3$Cl$_3$].



Operation of irradiation cell: (1), cell under vacuum (S3 and S4 closed); (2), S1 and S2 open to degas methanol; (3), S1 closed; (4), S3 open and dewar of propanol–dry ice placed around the cell; (5), when all photoproduct has dissolved and passed through sinter, S2 and S3 closed; (6), cell removed; (7), cell placed on N_2 line, S3 opened to the line, then S4; (8), syringe needle inserted through S4 and solution from cell syringed into the n.m.r. tube under N_2; (9), n.m.r. tube sealed and spectrum recorded

(ii) The complex (*ca.* 0·20 g) was irradiated for 3 days under an atmosphere of chlorine, after which time the solid was slightly darker than the starting material. The product was separated from the starting material as described in (*i*). The electronic spectrum of the filtrate had λ 420 nm {*cf.* 425 nm for *mer*-[Rh(py)$_3$Cl$_3$]}. I.r. absorptions of the solid obtained by evaporating the chloroform are compared with values for the trichloro-isomers in Table 2.

(c) *With dioxygen*. The complex *mer*-[Rh(py)$_3$(ox)Cl] (*ca.* 0·3 g) was irradiated in an atmosphere of oxygen for 3 days in a test tube. The product appeared to be slightly unstable since a small amount of pyridine could be detected. Water was added to the mixture and chlorine was bubbled through the yellow filtrate for 5 min by which time the solution had become deep blue. The water was removed *in vacuo*; the blue solid obtained was purified by stirring it in acetone. The blue crystals were collected and analysed. The experiment was repeated: agreement in the analyses was taken as a test for purity of the solid (its electronic spectrum in water showed λ 610 nm).

RESULTS AND DISCUSSION

Halogeno-oxalatotripyridinerhodium(III) *Complexes: Preparation and Properties*.—Chloro-oxalatotripyridinerhodium(III) (IV) was first prepared by Tchugaev[4] by the action of potassium oxalate on a boiling aqueous solution of *trans*-dichlorotetrapyridinerhodium(III) chloride. It may also be obtained through the interaction of rhodium(III) trichloride, pyridine, and potassium oxalate. The former method has also been applied[5] to the synthesis of the bromo-analogue (V), the formation of which is marginally easier in aqueous solution than that of the chloride.

TABLE 2

Comparison of the i.r. spectra (cm^{-1})[a] of the reaction product with literature values for isomers of the complex $[Rh(py)_3Cl_3]$

Product	*mer*-$[Rh(py)_3Cl_3]$	*fac*-$[Rh(py)_3Cl_3]$
1 608s	1 610s	
1 238w	1 240w	
1 210s	1 216s	
1 155w	1 158w	
1 070 1 065 } s	1 068s	
1 018m	1 019w	
783s	783s	782w
765s	763s	768s
755s	756s	761s
703sh	700sh	702s
698s	694s	693s
690s	687s	687s
358s	358s	
336s	334s	
298m	297m	
268s	267s	
249s	249s	
236m	236m	
185m	185m	

[a] s = Sharp, m = medium, w = weak, and sh = shoulder.

The oxalato-complexes (IV) and (V) are insoluble in most common solvents, but dissolve to some extent in aqueous pyridine or dimethyl sulphoxide. The complex $[Rh(py)_3Cl(ox)]$ was shown[3] to be insoluble in water or pyridine, but in a 50% v/v mixture these acted synergically to give a 0·0013M solution of the complex. Reaction (1) is, predictably, subject to catalysis, and

$$[Rh(py)_4X_2]^+ + ox \longrightarrow [Rh(py)_3X(ox)] + X^- + py \quad (1)$$

quantitative yields of complexes (IV) and (V) may be obtained conveniently *via* the action of a trace of sodium tetrahydroborate on an aqueous solution of the reactants. The 4-methylpyridine and 3,5-lutidine analogues are obtained similarly, the former in lesser yield, since it crystallizes from water as the water-soluble tetrahydrate. The four molecules of water are removable by vacuum desiccation at room temperature.

The complexes $[Rh(py)_3X(ox)]$ are kinetically quite inert, although a solution of (IV) in aqueous pyridine may slowly hydrolyse, while a solution in 10M-H_2SO_4 certainly does so, and (V) is slightly less stable in this medium where loss of oxalate is more probable. The aqueous pyridine solution of complex (IV) is unaffected by addition of sodium bromide or iodide, but again, a trace of sodium tetrahydroborate catalyses substitution of the halide ligand, and this is the method utilized for the preparation of the complex $[Rh(py)_3I(ox)]$, (VI). An attempt to prepare the complex $[Rh(py)_3(N_3)(ox)]$ by this method gave a product which still contained much (IV), while more forcing conditions produced only $[Rh(py)_3(N_3)_3]$.

TABLE 3

Selected vibrational bands of oxalato-complexes, $[Rh(py)_3X(ox)]$

Complex	Raman	I.r.	Assignment
(IV)	220s	226s	ν(Rh–py)
	277s	275s	
	317s	316s	
	356s	356vs	ν(Rh–Cl), (OCO)
		408m	ν(Rh–O)
	557s	556s	ν(Rh–O)[a]
		1 668vs	ν(C=O)
		1 700vs	
		1 722sh	
(V)	199s	197vs	ν(Rh–Br)
	231s	231s	ν(Rh–py)
		274m	
		312s	
		345vs	δ(OCO)
		359vs	
		396m	Chelate-ring deformations
		407m	
		465m	
		535w	ν(Rh–O)[a]
		554s	
		1 672vs	ν(C=O)
		1 705vs	
(VI)[b]		222s	ν(Rh–py)
		271s	
		311s	
		356vs	Chelate-ring deformations
		409m	
		465m	
		555s	ν(Rh–O)[a]
		1 668vs	ν(C=O)
		1 702vs	
(VII)	212s		ν(Rh–py)
	270s		
	313s		
	354m		
		465m	
		529s	δ(C–D)
		540s	
		554s	
	557s		ν(Rh–O)[a]
	985vs		py Ring breathing
	1 673m	1 667vs	ν(C=O)
	1 697m	1 700vs	

[a] Not purely (Rh–O). [b] Too deeply coloured to obtain a satisfactory Raman spectrum. Limit of observation in i.r., 200 cm^{-1}. [c] $[^2H_5]$py Complex.

Reliable assignment of bands in the vibrational spectra (Table 3) is difficult, as low-frequency transitions involving metal–ligand stretching and bending coordinates will be heavily coupled with deformation modes of the chelating oxalate ion. The low local symmetry (C_s) of the rhodium ion leads to all vibrations being both i.r.- and Raman-active. Even in complex (IV), the ν(Rh–Cl) absorption is probably obscured in the i.r. spectrum as (V) also has two strong bands in the appropriate region (340, 355 cm^{-1}) and (VI) one (356 cm^{-1}). However, the strong Raman–i.r. coincidence at 356 cm^{-1} may be attributed to ν(Rh–Cl). Replacement of chloride by bromide [(IV) ⟶ (V)] has the effect of producing a strong new band at 198 cm^{-1} in

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[5] P. Poulenc, *Ann. Chim.* (*France*), 1935, **4**, 634.

the Raman and i.r. spectra which is probably due to ν(Rh–Br). In the region 400—4 000 cm^{-1} i.r. spectra of (IV)—(VI) are virtually superimposable, and they are very similar between 200 and 400 cm^{-1} also. The tentative assignments of Table 3 follow the work[6] of Hester and Plane and earlier work here.[7] The [$^2H_5$]-pyridine analogue of the chloro-complex is included as complex (VII). The transition at *ca.* 550 cm^{-1} is assigned as being mainly ν(Rh–O), but, like the bands below it in energy, is probably not a simple fundamental. The i.r. absorption at *ca.* 315 cm^{-1} occurs in nearly all the pyridine complexes of rhodium, but the Raman activity at this energy in the oxalato-complexes suggests that it may here be coupling with a vibration of the chelating ligand. A band at 440—500 cm^{-1} has previously been attributed[6] to an oxalate deformation. Deuteriation of the pyridine ring removes the pyridine ring mode in this region to lower energy, but a medium-intensity band indeed remains at 465 cm^{-1}; it is absent in the absence of oxalate, while crystalline $K_2C_2O_4,2H_2O$ has a Raman band at 473 cm^{-1}.

Preparations of Complexes of 1,2-*Diaminoethane*.—Uncatalysed nucleophilic substitution by oxalate ion in the ion *trans*-[Rh(en)$_2$Cl$_2$]$^+$ occurs slowly; several hours of heating under reflux are required before any significant change in the electronic spectrum is noticeable. The addition of small amounts of a strong reducing agent ($NaBH_4$), however, leads to immediate reaction, easily noted by the colour change of the solution (yellow-orange to pale yellow). After a short period of heating under reflux, and the addition of $LiClO_4$, the complex [Rh(en)$_2$(ox)]ClO$_4$ can be isolated in good yield. A strong reducing agent is necessary, for ethanol, hydrazine, or sodium hypophosphite did not lead to the isomerization catalysed by tetrahydroborate ion. The isomerization about the Rh^{III} centre is not limited to the oxalate ion; the complexes [Rh(en)$_2$(mal)]NO$_3$, [Rh(en)$_2$(gly)]S$_2$O$_6$, [Rh(en)$_2$(ala)]S$_2$O$_6$, and [Rh(en)$_3$](ClO$_4$)$_3$ have been prepared by similar reactions.

The complex [Rh(en)$_2$(ox)]ClO$_4$ is a convenient starting material for the preparation of ions of the *cis*-[Rh(en)$_2$X$_2$]$^+$ series. For example, a short (2—3 min) period of heating under reflux of [Rh(en)$_2$(ox)]ClO$_4$ with HCl or HBr leads to *cis*-[Rh(en)$_2$Cl$_2$]$^+$ and *cis*-[Rh(en)$_2$Br$_2$]$^+$ respectively, which are easily isolated as their halide salts. Decomposition of the complex [Rh(en)$_2$(ox)]ClO$_4$ with perchloric acid presumably yields *cis*-[Rh(en)$_2$(H$_2$O)$_2$]$^{3+}$ in solution, although no attempt was made to isolate this species.* Electronic spectra of the complexes prepared by these methods are reported in SUP 20858 and are compared with available data from the literature. I.r. spectra of all complexes prepared here agreed with published data, or corresponded with those of analogous complexes of cobalt(III).

To date, the best synthetic path to the *cis*-[Rh(en)$_2$X$_2$]$^+$ series of complexes has been through initial preparation of *cis*-[Rh(en)$_2$Cl$_2$]$^+$ by the method[1] of Johnson and Basolo. This provides an excellent route † to the salt *trans*-[Rh(en)$_2$Cl$_2$]NO$_3$, but, in our hands, the yields of the *cis*-isomer have been variable and low. A modification of the original preparation gives increased yields of the *cis*-isomer (see Experimental section). The short time of heating under reflux minimizes the thermal isomerization to the *trans*-isomer, and careful control of pH prevents rapid base hydrolysis of *cis*-[Rh(en)$_2$Cl$_2$]$^+$. Use of Na$_3$[RhCl$_6$] rather than RhCl$_3$,3H$_2$O has no obvious theoretical foundation, and is recommended solely because it gives increased yields of the *cis*-isomer. Contamination of *cis*-[Rh(en)$_2$Cl$_2$]NO$_3$, by its *trans*-isomer, however, is still difficult to avoid.

A better path to the salt *cis*-[Rh(en)$_2$Cl$_2$]Cl is to heat the complex [Rh(en)$_2$(ox)]ClO$_4$ under reflux with HCl, for no detectable contamination by the *trans*-isomer then occurs. Loss of co-ordinated oxalate is favoured by acids, since [Rh(en)$_2$(ox)]ClO$_4$ does not react when heated under reflux for 30 min in 1M-NaOH solution. Such replacements of oxalate are well known. For example, the synthesis of the complex *cis*-[Ru(py)$_4$Cl$_2$], recently reported[8] by Raichait and Taube, involved decomposition by HCl of [Ru(py)$_4$(ox)]; similarly, attack on [Rh(py)$_3$(ox)Cl] by HCl cleanly leads[3] to *fac*-[Rh(py)$_3$Cl$_3$]. Numerous applications in cobalt(III) chemistry have been made.

A synthesis of the ion [Rh(en)$_2$(ox)]$^+$ has been reported,[9] but the low yields (6%) and long reaction time (18 h) do not recommend it as a general route. The catalytic method reported here is rapid (30 min) and electronic spectra show essentially complete conversion of *trans*-[Rh(en)$_2$Cl$_2$]$^+$ to [Rh(en)$_2$(ox)]$^+$, with the yield of isolatable solid limited only by the solubility of the particular salt. We discuss the mechanistic implications of the catalysed stereo-change (*trans* ⟶ *cis*) elsewhere.

Several amino-acid complexes of Rh^{III}, including [Rh(en)$_2$(gly)]$^{2+}$ and [Rh(en)$_2$(ala)]$^{2+}$, have been described,[10] as their iodide, by Waller *et al.* Hall and Douglas have reported[11] using that synthesis, which involves ethanol-catalysed substitution of an amino-acid into either *cis*- or *trans*-[Rh(en)$_2$Cl$_2$]$^+$, but our own efforts and those of others here[12] to repeat this synthesis have been unsuccessful. We make no effort to explain this difference in results, but offer the syntheses reported here as reliable alternative preparations.

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* Two of us (R. D. G. and L. R. H. T.) are using changes of circular dichroism in the optically active species to evaluate pK_1 and pK_2 for this complex.

† We have also re-examined the alternative route[3] to the *trans*-isomer *via* *trans*-[Rh(py)$_4$Cl$_2$]$^+$ + 2en ⟶ *trans*-[Rh(en)$_2$Cl$_2$]$^+$ + 4py and have now characterized the intermediate *trans*-[Rh(en)(py)$_2$Cl$_2$]$^+$. (Details are given in the Experimental section.)

[6] R. E. Hester and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 513.

[7] R. D. Gillard, S. H. Laurie, and P. R. Mitchell, *J. Chem. Soc.* (*A*), 1969, 3007.

[8] D. U. Raichait and H. Taube, *Inorg. Chem.*, 1972, **11**, 999.

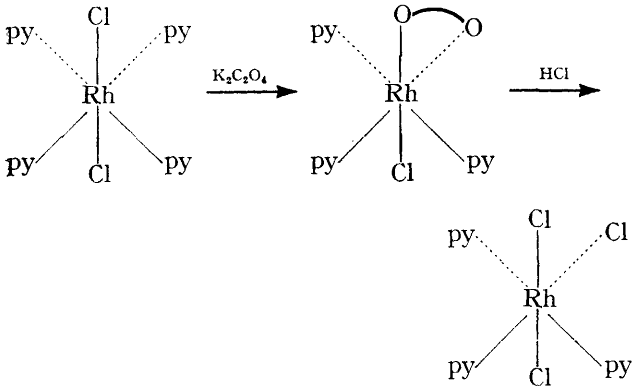
[9] T. P. Dasgupta, R. M. Milburn, and L. Damrauer, *Inorg. Chem.*, 1970, **9**, 2789.

[10] J. F. Waller, jun., J. Hu, and B. E. Bryant, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2371.

[11] S. K. Hall and B. E. Douglas, *Inorg. Chem.*, 1968, **7**, 530.

[12] M. E. Sheridan, personal communication; F. Topp, personal communication.

Reaction of Oxalatopyridine Complexes with Hydrohalogenic Acids.—It has been found previously[3] that the complex (IV), dissolved in concentrated hydrochloric acid, slowly deposits orange crystals of $[Rh(py)_3Cl_3]$, which Delépine made[13] by treating aqueous hexachlororhodate(III) with pyridine. As the chloro-oxalate (IV) is the uncharged complex formed from the ion $[Rh(py)_4Cl_2]^+$, of known *trans*-structure, the stereochemical rigidity of rhodium(III) complexes implies that the trichloride can only be the *mer*-isomer.



This complex is also formed when insufficient pyridine is used in the ethanol-catalysed preparation of *trans*-$[Rh(py)_4Cl_2]Cl$, especially if pyridine is added to the rhodium(III) solution *before* the ethanol. However, none of the *fac*-isomer is isolatable under these conditions, whereas Collman and Holtzclaw obtained[14] both isomers (without catalysis); the *mer*-isomer they referred to as their 'orange-brown' isomer. This is the product obtained when *trans*-$[Rh(py)_4Cl_2]Cl$ is heated for a considerable time in either ethanol or neat pyridine. It seems that equilibrium (2) is influenced

$$trans\text{-}[Rh(py)_4Cl_2]^+ + Cl^- \rightleftharpoons mer\text{-}[Rh(py)_3Cl_3] + py \quad (2)$$

strongly by the ability of the given medium to solvate the chloride ion involved; hence it is displaced to the right in pyridine, despite that reagent's excess.

Reactions (3) and (4) occur as written when the

$$mer\text{-}[Rh(py)_3Cl(ox)] + 2HBr \longrightarrow mer\text{-}[Rh(py)_3ClBr_2] + H_2ox \quad (3)$$

$$mer\text{-}[Rh(py)_3Br(ox)] + 2HCl \longrightarrow mer\text{-}[Rh(py)_3Cl_2Br] + H_2ox \quad (4)$$

chloro- or bromo-oxalato-complexes are dissolved in warm hydrobromic or hydrochloric acids, respectively. The products, $[Rh(py)_3ClBr_2]$ (VII) and $[Rh(py)_3Cl_2Br]$ (VIII), are obtained quantitatively as deep red and deep orange crystals, respectively, and purified by recrystallization from chloroform.

Mixed halogeno-complexes of the heavier metals are not yet common. The complexes (VII) and (VIII) with both chloride and bromide co-ordinated are the first well characterized species with both halogens bonded to the same rhodium atom in an uncharged complex. Electronic spectral data for the trihalogenotripyridine complexes are in SUP 20858. Substitution of chloride by bromide progressively lowers the energy of the first absorption band in a monotonic fashion.

Photochemistry.—Poulenc remarked[5] that the yellow oxalato-complexes $[Rh(py)_3(ox)X]$ were photosensitive, the solids becoming red in daylight. He further noted that the red photoproduct was soluble in several organic liquids (in contrast to the reactant, which is insoluble in most solvents). The oxalato-chlorocomplex we have found to be thermally stable as a solid to *ca.* 280 °C. From measurements of the amounts and nature of the gas evolved, we define the photodecomposition as an intramolecular reduction of rhodium(III) by oxalate ion. Two moles of carbon dioxide are produced for every mole of rhodium(III) complex lost [equation (5)]. We

$$mer\text{-}[Rh(py)_3(ox)X] \xrightarrow{h\nu} [Rh(py)_3X] + 2CO_2 \quad (5)$$

have not yet been able to characterize the extremely reactive rhodium(I) species by direct elemental analysis. However, the n.m.r. spectrum in the pyridine region of the product at room temperature was characteristic of a Rh^I complex [τ 1·65 (α), 2·55 (β), and 2·05 (γ)].

The complex $[Rh(py)_3Cl]$ is very readily oxidized: instead of forming a red solution on being dissolved in degassed methanol {*cf.* $[Rh(PPh_3)_3Cl]$} it reacts to form a dark yellow solution. Its chemical reactions include (*a*) its oxidation by dichlorine, hydrogen chloride, dihydrogen, and dioxygen, and (*b*) substitutions by phosphines and carbon monoxide.

(a) We find that oxidative addition of chlorine occurs [equation (6)] in which the product, a well known

$$[Rh(py)_3Cl] + Cl_2 \longrightarrow mer\text{-}[Rh(py)_3Cl_3] \quad (6)$$

complex, was identified by its electronic and far i.r. spectrum. It matters not whether dichlorine is present throughout the irradiation, or is added to the product of irradiation in vacuum, the product is the same. In the same way, we find that, in dichloromethane, the yellow solution of chlorotris(4-methylpyridine)oxalatorhodium(III) evolves gas on irradiation, and gives a brown solution of the rhodium(I) species, which, with dichlorine, gives the known *mer*-tris(γ-picoline) complex [equation (7)].

$$mer\text{-}[Rh(\gamma\text{-}pic)_3(ox)Cl] \xrightarrow{h\nu} 2CO_2 + [Rh(\gamma\text{-}pic)_3Cl] \xrightarrow{Cl_2} mer\text{-}[Rh(\gamma\text{-}pic)_3Cl_3] \quad (7)$$

With dioxygen, the reduced rhodium species combines to give a product which, on treatment with dichlorine, became bright blue, showing an electronic spectrum (λ 610 nm) characteristic of superoxorhodium(III)

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[13] M. Delépine, *Bull. Soc. chim. France*, 1929, **45**, 235.

[14] J. P. Collman and H. F. Holtzclaw, *J. Amer. Chem. Soc.*, 1959, **81**, 2054.

complexes described previously.[15] The stoicheiometry has not yet been fully evaluated.

(b) Substitution by triphenylphosphine in the presence of formaldehyde also offers strong support for the rhodium(I) formulation, since the product is the known complex $[Rh(PPh_3)_2(CO)Cl]$.

While photochemical reactions of oxalato-complexes have been widely studied and used, this is most true of the radical-type 'non-complementary' one-electron systems (such as those involving ions of first-row transition elements). Many distinctive behaviours of the heavier second- and third-row transition-metal ions (*e.g.*, hydrogenation) involve their two-electron redox character, and the reaction with oxalate is no exception. We know, as yet, only a few photochemical reactions of this kind [equations (8)—(10)].* It seems probable that the reduced metal complexes produced in (10) will

$$[Pd(NH_3)_2(ox)] \longrightarrow \text{`}[Pd(NH_3)_2]\text{'}(?) + 2CO_2 \longrightarrow Pd^0 \text{ (black) (ref. 16)} \quad (8)$$

$$[Pt(PPh_3)_2(ox)] \longrightarrow \text{`}[Pt(PPh_3)_2]\text{'} \longrightarrow \text{products (ref. 17)} \quad (9)$$

$$[RhL_3Cl(ox)] \longrightarrow [RhL_3Cl] + 2CO_2 \quad (10)$$

prove useful as nitrogen-ligand analogues of Wilkinson's catalyst; this is borne out by reactions (11) and (12) which carry the pyridine complexes into the phosphine

$$[Rh(py)_3Cl] + 3PPh_3 \longrightarrow [Rh(PPh_3)_3Cl] + 3py \quad (11)$$

$$[Rh(py)_3Cl] + 2PPh_3 + HCHO \longrightarrow [Rh(PPh_3)_2(CO)Cl] + 3py + H_2 \quad (12)$$

series. We shall describe other rhodium(I) pyridine complexes elsewhere.

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* The purple colour of the complex $[Rh(phen)_3]_2(C_2O_4)_3,xH_2O$ noted by E. D. McKenzie (M.Sc. Thesis, University of Queensland, Brisbane, 1958) is probably related, and the photoreaction of $[Co(phen)_2(ox)]^+$ may be similar (C. H. Langford, personal communication).

[15] A. W. Addison and R. D. Gillard, *J. Chem. Soc.* (*A*), 1970, 2523.

[16] F. G. Mann, D. C. Crowfoot, D. C. Gattiker, and N. Wooster *J. Chem. Soc.*, **1935**, 1642.

[17] D. M. Blake and C. J. Nyman, *Chem. Comm.*, 1969, 483; *J. Amer. Chem. Soc.*, 1970, **92**, 5359.