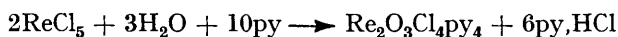


500. *Amine Complexes of Rhenium(v).*

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We have prepared μ -oxodioxotetrahalogenotetrakis(pyridine)dirhenium(v), $\text{Re}_2\text{O}_3\text{X}_4\text{py}_4$ (X = Cl or Br), and the analogous bipyridyl compound (X = Cl), and have shown that the pyridine compound is an intermediate in the conversion of *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$ into *trans*- $[\text{ReO}_2\text{py}_4]\text{Cl}$. The ethoxo-compound $\text{ReOCl}_2(\text{OEt})\text{py}_2$ has been prepared.

THE compound μ -oxodioxotetrachlorotetrakis(pyridine)dirhenium(v), $\text{Re}_2\text{O}_3\text{Cl}_4\text{py}_4$, has been prepared as green needles by the action of excess of pyridine on a solution of rhenium pentachloride in acetone. No especial precautions were taken to dry the acetone or pyridine so that a reaction such as:



is the most likely explanation for the formation of the oxo-complex. The pyridine complex gives a non-conducting solution in nitrobenzene and it is diamagnetic in the solid state.

Since we have shown ¹ that *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$ reacts with excess of pyridine in boiling ethanol in air to form the orange complex *trans*- $[\text{ReO}_2\text{py}_4]\text{Cl}$, it seemed likely that the

Johnson, Lock, and Wilkinson, *J.*, 1964, 1054.

green oxo-pyridine compound was an intermediate in this reaction. This was confirmed by treating a suspension of *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$, in benzene, with wet pyridine (2 moles per g.-atom Re) at 20° , when a green oxo-complex, identical with that prepared above, was precipitated:

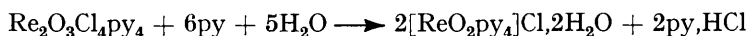


The analogous bromo-complex, $\text{Re}_2\text{O}_3\text{Br}_4\text{py}_4$, was prepared similarly from $\text{ReOBr}_3(\text{PPh}_3)_2$.

The addition of wet pyridine to a suspension of $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ in benzene gave a purple solution which deposited the green oxo-complex identical with that prepared above.

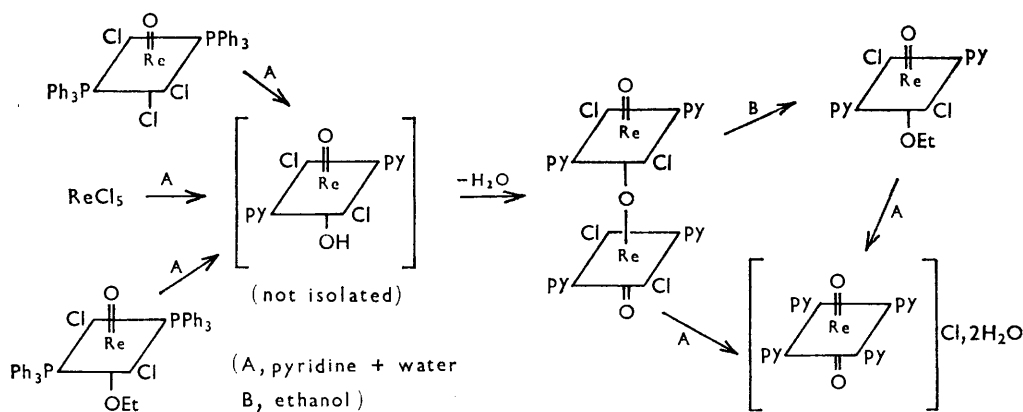
It seemed reasonable to assume that in these reactions an intermediate hydroxy-species, $\text{ReO}(\text{OH})\text{Cl}_2\text{py}_2$, is formed, through displacement of the labile chloride ion *trans* to the oxo-group, which gives the μ -oxo-complex by loss of water. Although such a hydroxy-species has not been isolated, the corresponding ethoxy-complex can be obtained (see below).

In a further reaction with excess of moist pyridine in ethanol, the green oxo-chloro-complex formed the dioxo-complex $[\text{ReO}_2\text{py}_4]\text{Cl}, 2\text{H}_2\text{O}$, identical with that prepared from the phosphine complex:¹



The oxo-bridge structure proposed for the green oxo-halogeno-complexes is similar to that found in the $[\text{Re}_2\text{OCl}_{10}]^{4-}$ ion² and proposed for the bipyridyl complex of molybdenum(v), $\text{Mo}_2\text{O}_3\text{Cl}_4\text{bipy}_2$.³ A 2,2'-bipyridyl complex, $\text{Re}_2\text{O}_3\text{Cl}_4\text{bipy}_2$, can be obtained from rhenium pentachloride by a method analogous to that used for the pyridine complex; the ligand nitrogen atoms must necessarily be *cis* here rather than *trans*, the configuration which we have assumed for the pyridine complexes in the Figure.

The oxo-bridge of the green chloro-pyridine complex could be cleaved by ethanol; on heating in ethanol, the blue ethoxo-complex $\text{ReOCl}_2(\text{OEt})\text{py}_2$ was obtained. In a further reaction with excess of moist pyridine, the blue ethoxo-complex gave the dioxo-complex *trans*- $[\text{ReO}_2\text{py}_4]\text{Cl}, 2\text{H}_2\text{O}$, identical with that prepared previously. The reactions are summarised in the Figure.



Reactions of phosphine and pyridine complexes of rhenium. The *trans* stereochemistries for pyridine and chlorine of $\text{Re}_2\text{O}_3\text{Cl}_4\text{py}_4$ and $\text{ReOCl}_2(\text{OEt})\text{py}_2$ are assumed.

These amine μ -oxodioxo- and oxoethoxo-complexes have a strong infrared band between 900 and 1000 cm^{-1} , which is assigned to the $\text{Re}=\text{O}$ stretching mode.¹ The ethoxo-complex

² Morrow, *Acta Cryst.*, 1962, **15**, 851; Jezowska-Trzebiatowska and Wojciechowski, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1477.

³ Mitchell, *J. Inorg. Nuclear Chem.*, 1963, **25**, 963.

has a very strong band at 920 cm.^{-1} which is assigned to the δOCH_2 vibration by comparison with the similar oxoethoxytriphenylphosphine complexes.¹ In $\text{Re}_2\text{O}_3\text{Cl}_4\text{py}_4$, we were unable to characterise any frequency for the bridging oxygen atom.

EXPERIMENTAL

Microanalyses were performed by the Microanalytical Laboratory, Imperial College. Molecular weights were determined at 37° in acetone solution, using a Mechrolab Osmometer. Infrared spectra were recorded on Nujol mulls, using a Perkin-Elmer model 21 or a Grubb-Parsons Spectromaster spectrometer. Magnetic measurements were made by the Gouy method at 20° .

μ -Oxidioxotetrachlorotetrakis(pyridine)dirhenium(v).—Method A. Pyridine (15 ml.) was added to a solution of rhenium pentachloride (2.0 g.) in acetone (reagent grade; 30 ml.). The precipitate was collected, dissolved in dichloromethane, and reprecipitated with light petroleum (b. p. $30\text{--}40^\circ$) as green needles (0.5 g., 20%), m. p. 230° (Found: C, 27.3; H, 2.2; N, 6.2; O, 5.5; Cl, 16.0; Re, 42.0%; *M*, 871. $\text{C}_{20}\text{H}_{20}\text{Cl}_4\text{N}_4\text{O}_3\text{Re}_2$ requires C, 27.3; H, 2.3; N, 6.4; O, 5.5; Cl, 16.1; Re, 42.4%; *M*, 879), ν_{max} 972 cm.^{-1} . The compound was sparingly soluble in pyridine, acetone, dichloromethane, and chloroform and was insoluble in benzene, alcohol, water, carbon tetrachloride, and diethyl ether.

Method B. A solution of water in pyridine (6.7%; 0.24 ml.) was added to a suspension of *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$ ¹ (0.83 g.) in benzene (50 ml.) under nitrogen, and the mixture was shaken at 20° for 12 hr. The precipitate was washed with benzene, methanol, and diethyl ether, and then dissolved in dichloromethane and reprecipitated with light petroleum (b. p. $40\text{--}60^\circ$) as green needles (0.38 g., 86%) (Found: C, 27.3; H, 2.5; O, 5.4%; *M*, 844).

Method C. As for method B, except that $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ ¹ (0.83 g.) was used instead of *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$. Yield, 0.13 g. (34%) (Found: C, 27.7; H, 2.8; N, 6.4; O, 5.5%).

μ -Oxidioxotetrachlorobis(2,2'-bipyridyl)dirhenium(v).—A solution of 2,2'-bipyridyl (1.0 g.) in acetone (10 ml.) was added to rhenium pentachloride (2.0 g.) in acetone (10 ml.). The collected precipitate was extracted with cold acetone, and the green solution was evaporated to dryness to give green microcrystals (0.5 g., 20%) (Found: C, 27.0; H, 2.7; N, 6.4. $\text{C}_{20}\text{H}_{18}\text{Cl}_4\text{N}_4\text{O}_3\text{Re}_2$ requires C, 27.4; H, 2.0; N, 6.4%; ν_{max} 930 cm.^{-1} . The solubility of this compound was similar to that of the pyridine complex described above.

μ -Oxidioxotetrabromotetrakis(pyridine)dirhenium(v).—A solution of water in pyridine (6.7%; 0.29 ml.) was added to a suspension of $\text{ReOBr}_3(\text{PPh}_3)_2$ ¹ (1.0 g.) in dry benzene (10 ml.) under nitrogen. The mixture was shaken for $1\frac{1}{2}$ hr. and allowed to stand at 20° for 16 hr. The product was collected and reprecipitated from dichloromethane with light petroleum (b. p. $30\text{--}40^\circ$) as green plates (0.37 g., 69%), m. p. $215\text{--}222^\circ$ (decomp.) (Found: C, 22.7; H, 1.95; O, 4.6%; *M*, 1085. $\text{C}_{20}\text{H}_{20}\text{Br}_4\text{N}_4\text{O}_3\text{Re}_2$ requires C, 22.4; H, 2.1; O, 4.5%; *M*, 1056), ν_{max} 971 cm.^{-1} .

Oxidichloroethoxobis(pyridine)rhenium(v).—A suspension of $\text{Re}_2\text{O}_3\text{Cl}_4\text{py}_4$ (0.1 g.) in dry ethanol (25 ml.) was refluxed for 3 days. On cooling, the product separated as blue plates (0.025 g., 25%), m. p. $182\text{--}184^\circ$ (decomp.) (Found: C, 30.4; H, 3.0; N, 6.0; O, 6.8%; *M*, 476. $\text{C}_{12}\text{H}_{15}\text{Cl}_2\text{N}_2\text{O}_2\text{Re}$ requires C, 30.3; H, 3.2; N, 5.9; O, 6.7%; *M*, 476), ν_{max} 962 and 920 cm.^{-1} .

Action of Pyridine on μ -Oxidioxotetrachlorotetrakis(pyridine)dirhenium(v).—A suspension of $\text{Re}_2\text{O}_3\text{Cl}_4\text{py}_4$ (0.5 g.) in ethanol (25 ml.) was heated under reflux with pyridine (5 ml.) for $\frac{1}{2}$ hr. Diethyl ether was added to the orange solution to precipitate dioxotetrakis(pyridine)rhenium(v) chloride dihydrate as orange prisms (0.24 g., 34%) (Found: C, 39.7; H, 3.9. Calc. for $\text{C}_{20}\text{H}_{26}\text{ClN}_5\text{O}_4\text{Re}$: C, 39.6; H, 4.0%).

Action of Pyridine on Oxidichloroethoxobis(pyridine)rhenium(v).—A solution of $\text{ReOCl}_2(\text{OEt})\text{py}_2$ (5 mg.) in pyridine (1 ml.) containing water (1 drop) was boiled for 10 min. On cooling, dioxotetrakis(pyridine)rhenium(v) chloride dihydrate separated as orange needles (4 mg., 55%). The infrared spectrum of this compound was identical with that of an authentic sample.¹