Studies on Transition-Metal Oxo and Nitrido Complexes. Part 11.[1] New Oxo Complexes of Ruthenium as Aerobically assisted Oxidants, and the X-Ray Crystal Structure of [Ru2O6(py)4]·3.5H2O†

Andrew C. Dengel, Ahmed M. El-Hendawy, William P. Griffith,* Caroline A. O'Mahoney, and David J. Williams*
Inorganic and Chemical Crystallographic Laboratories, Imperial College of Science, Technology and Medicine, London SW7 2AY

The new complexes [Ru2O6L4] [L = 4-t-butylpyridine (4But-py), nicotinic acid (Hnic), isonicotinamide (isna), pyridine-2-carboxylic acid (Hpyca), $or \frac{1}{2}$ (2,2'-bipyridyl) (bipy)] have been prepared and the X-ray crystal structure of another member of the series, [Ru2O6(py)4]·3.5H2O, determined [triclinic, space group $P\bar{1}$, a = 7.943(1), b = 8.952(2), c = 9.257(3) Å, α = 98.76(2), β = 95.75(2), γ = 98.08(1)°, Z = 1, R = 0.065]. New complexes are also reported of the types trans-[RuO2L4]$^{2+}$ [L = Hnic, Hpyca, or pyridine-3,4-dicarboxylic acid (H2pydca)], trans-[RuO2Cl2L2] (L =4But-py or 4-chloropyridine, trans-[RuO2(pyca)2] and trans-[RuO2Cl3L]$^-$ (L = py, 4But-py, 3-methylpyridine, or 3,4-dimethylpyridine). Vibrational spectra, structures, and reactions of these species are discussed: they function as overall four-electron oxidants (eight-electron in the case of [Ru2O6L4]), converting primary alcohols into aldehydes and secondary alcohols into ketones, and function catalytically with N-methylmorpholine N-oxide or iodosylbenzene as co-oxidant. The most soluble of them, trans-[Ru2O6(py)4]·3.5H2O, trans-[Ru2O6(4But-py)4], trans-[RuO2(py)4]$^{2+}$, and trans-[RuO2Cl3(4But-py)]$^-$, will also effect such oxidation of alcohols with dioxygen as co-oxidant.

We have shown that oxo complexes of ruthenium(VI)[1–3] and -(VII)[4–6] are effective oxidants for alcohols, primary alcohols giving aldehydes[1,4–6] or carboxylic acids[2,3] and secondary alcohols giving ketones,[1–6] often with considerable selectivity.[3,5] In the preceding paper of this series[1] we suggested, on the basis of vibrational spectra, that the reported 'RuO4(py)2'[7,8] (py = pyridine) is in fact a ruthenium(VI) dimer, [Ru2O6(py)4], and that both it and trans-[RuO2(py)4]$^{2+}$ are efficient overall four-electron oxidants of alcohols to aldehydes or ketones. In this paper we give the X-ray crystal structure of [Ru2O6(py)4]·3.5H2O, report a number of new oxoruthenium(VI) complexes with substituted pyridines and analogous ligands, and show that some of them will function as aerobically assisted oxidants for alcohols.

Results and Discussion

(a) *Complexes of the Type* [Ru2O6L4].—(i) *Preparation and X-ray crystal structure of* [Ru2O6(py)4]·3.5H2O. It has been reported that reaction of ruthenium tetraoxide (RuO4) with pyridine in carbon tetrachloride gives an ill defined material 'RuO4(py)2'[7,8] subsequently reformulated on the basis of the i.r. spectrum of the material as [RuO2(OH)2(py)2].[9,10] On the basis of Raman and i.r. studies we tentatively reformulated 'RuO4(py)2' as [Ru2O6(py)4], having prepared it by reaction of RuO4 vapour with ice-cold aqueous pyridine or by reaction of trans-[RuO3(OH)2]$^{2-}$ with HpyCl.[1] By using a slight variant of the former method we have now succeeded in preparing small crystals of the material and have determined its X-ray crystal structure.
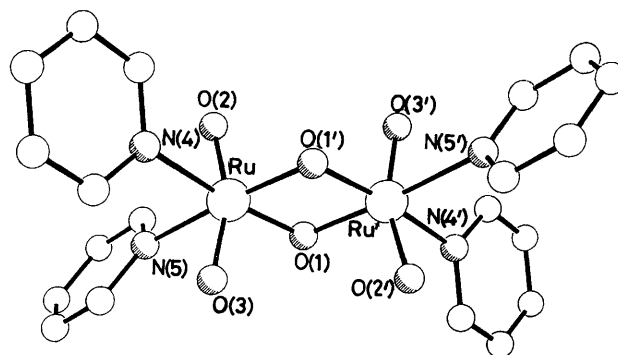

Figure. Perspective view of the structure of [Ru2O6(py)4] with atom labelling

The structure of the complex is shown in the Figure together with the atom labelling. Selected bond lengths and angles are given in Table 1 and the atomic co-ordinates, which include those of the water molecules of crystallisation, are given in Table 2. Despite experimental limitations on the available diffraction data (due to the small crystal size and rapid X-ray decomposition) the geometry about the ruthenium atoms is well defined. The complex is dimeric with a planar Ru2O2 bridge [Ru–O 1.93(1) Å] in which the Ru–O–Ru angle is 100.0(5)°. The terminal Ru=O bond length of 1.72(1) Å is comparable with those found for other 'ruthenyl' complexes subjected to X-ray study, viz. 1.732(8) Å in trans-NaK5[RuO2(HIO6)2]·8H2O,[2] 1.718(5) and 1.705(7) Å in the macrocyclic complexes trans-[RuO2(tmtacpd)][ClO4]2 (tmtacpd = 1,5,9,13-tetramethyl-1,4,8,12-tetra-azacyclopentadecane) and trans-[RuO2(tmtachd)][ClO4]2 (tmtachd = 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane),[11] 1.709(4) Å in trans-[N(PPh3)2]2[RuO2Cl4],[12] and 1.726(1) Å in trans-[RuO2(py)2(O2CMe)2].[13] In all these complexes however the

Table 1. Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[Ru_2O_6(py)_4]\cdot3.5H_2O$

Ru–O(1)	1.940(9)	Ru–O(2)	1.720(11)
Ru–O(3)	1.730(12)	Ru–N(4)	2.202(9)
Ru–N(5)	2.198(10)	Ru $\cdots$ Ru′	2.948(2)
O(1)–Ru′	1.909(10)		
O(1)–Ru–O(2)	96.8(4)	O(1)–Ru–O(3)	97.3(5)
O(2)–Ru–O(3)	160.5(4)	O(1)–Ru–N(4)	173.4(4)
O(2)–Ru–N(4)	82.2(4)	O(3)–Ru–N(4)	85.3(5)
O(1)–Ru–N(5)	94.8(5)	O(2)–Ru–N(5)	83.3(5)
O(3)–Ru–N(5)	82.1(5)	N(4)–Ru–N(5)	91.6(5)
O(1)–Ru–O(1′)	80.0(5)	O(2)–Ru–O(1′)	98.2(5)
O(3)–Ru–O(1′)	97.5(5)	N(4)–Ru–O(1′)	93.6(4)
N(5)–Ru–O(1′)	174.7(5)	Ru–O(1)–Ru′	100.0(5)

Table 2. Atom co-ordinates ($\times 10^4$) with e.s.d.s in parentheses

Atom	x	y	z
Ru	1 349(1)	1 275(1)	713(1)
O(1)	−493(14)	776(11)	−909(10)
O(2)	2 978(13)	895(11)	−311(11)
O(3)	231(13)	2 193(13)	1 996(13)
N(4)	3 413(14)	1 556(14)	2 554(9)
C(1)	3 377(14)	2 515(14)	3 885(9)
C(2)	4 705(14)	2 665(14)	5 029(9)
C(3)	6 068(14)	1 857(14)	4 844(9)
C(4)	6 104(14)	898(14)	3 514(9)
C(5)	4 776(14)	747(14)	2 369(9)
N(5)	2 125(15)	3 628(10)	340(17)
C(6)	1 877(15)	4 897(10)	1 327(17)
C(7)	2 284(15)	6 365(10)	1 000(17)
C(8)	2 938(15)	6 565(10)	−313(17)
C(9)	3 186(15)	5 296(10)	−1 299(17)
C(10)	2 780(15)	3 827(10)	−972(17)
O(11)	199(23)	1 124(27)	6 295(17)
O(12)	−259(32)	3 452(26)	4 983(24)
O(13)	611(39)	4 646(28)	6 302(25)

O=Ru=O angle is 180°, whereas in this species it is distinctly non-linear, the O=Ru=O angle being 160.5(4)°. The bending occurs away from the Ru_2O_2 bridge and towards the pyridine ligands, bisecting the angle between them. A similar distortion is observed in the structure of $[Os_2O_6(py)_4]$, the only other complex of comparable type $[Os–O \ 1.98(1) \ Å, \ Os=O \ 1.74(2) \ Å, O=Os=O \ 163.5(8)°, \ Os–N \ 2.21(2) \ Å]$.[14] This effect is likely to arise from electron pair–electron pair repulsion between the terminal oxo ligands and the oxygen atoms of the tightly bound Ru_2O_2 bridge; the Ru–O distance in the latter is relatively short, suggesting the presence of π bonding, and the O–Ru–O angle in this unit is slightly contracted at 80.5°. Deviations from planarity of the equatorial co-ordinating atoms are small with a maximum deviation of 0.03 Å [for O(1)]. The two pyridine rings are equally inclined to this plane by 69(1)°. Although the Ru $\cdots$ Ru distance is fairly short [2.948(2) Å] we do not believe there to be any substantial metal–metal bonding interaction. The water molecules of crystallisation are involved in hydrogen bonding to each other and also to O(1) and O(2).

(ii) Other complexes. These complexes [L = 4-t-butyl-pyridine(4Bu^t-py) or $\frac{1}{2}$(2,2′-bipyridyl)(bipy)] were prepared as red-brown solids from RuO_4 and the ligand in carbon tetrachloride; by using aqueous solutions of the ligand L′ [L′ = $\frac{1}{2}$bipy, Hnic, isna, or pyridine-2-carboxylic acid (Hpyca)] species of the form $[Ru_2O_6L'_4]\cdot nH_2O$ were obtained as brown solids. Apart from $[Ru_2O_6(4Bu^t-py)_4]$ the complexes have limited solubility in water or organic solvents. We suggest that they have the same basic structure as $[Ru_2O_6(py)_4]\cdot3.5H_2O$

on the basis of analytical data, vibrational spectra [see section (*c*) below] and their mode of preparation. Despite many attempts we were unable to prepare $[Ru_2O_6(phen)_2]$ (phen = 1,10-phenanthroline); there are reports on the formation of $[RuO_4(bipy)]$ and $[\{RuO_3(phen)\}_2O]$ from the reaction of RuO_4 in carbon tetrachloride with 2,2′-bipyridyl or 1,10-phenanthroline,[15] and of $[RuO_2(OH)_2(bipy)]\cdot3H_2O$ and $[\{Ru(OH)_3(phen)\}_2O]$ prepared from the above complexes in methanol.[16] It is possible that the species reported as $[RuO_4(bipy)]$[15] is identical to $[Ru_2O_6(bipy)_2]$.

(b) Complexes of the Type trans-$[RuO_2Cl_nL_{4-n}]^{2-n}$ (*n* = 0, 2, or 3).—We have previously reported the preparation of *trans*-$[RuO_2(py)_4]^{2+}$, made by reaction of *trans*-$[RuO_3(OH)_2]^{2-}$ in base with pyridine and HBF$_4$ or HPF$_6$.[1] Similar procedures using nicotinic acid, pyridine-2-carboxylic acid, or pyridine-3,4-dicarboxylic acid (H$_2$pydca) with a basic aqueous solution of *trans*-$[RuO_3(OH)_2]^{2-}$ followed by addition of HBF$_4$ gave *trans*-$[RuO_2L_4]^{2+}$ salts as yellow-brown materials, sparingly soluble in water and organic solvents.

Attempts to make species of the form *trans*-$[RuO_2Cl(L)_3]^+$ were unsuccessful, though reaction of RuO_4 with an aqueous solution of pyridine and HCl (Ru:py:Cl = 1:3:2) gave a green solid whose elemental analyses suggest a composition between *trans*-$[RuO_2(py)_4]^{2+}$ and *trans*-$[RuO_2Cl(py)_3]^+$. We have previously reported *trans*-$[RuO_2X_2(py)_2]$ (X = Cl [1,17] or Br [1]); a modification of the original method,[1] reaction of aqueous *trans*-$[RuO_3(OH)_2]^{2-}$ with a 1:1 mixture of 4-t-butylpyridine and HCl, gave the yellow, unstable *trans*-$[RuO_2Cl_2(4Bu^t-py)_2]\cdot H_2O$. Reaction of RuO_4 with aqueous 4-chloropyridine hydrochloride gave the more stable species *trans*-$[RuO_2Cl_2(4Cl-py)_2]$. The passage of RuO_4 into an aqueous solution of Hpyca yields an unstable brown solid for which analytical data are close to those for *trans*-$[RuO_2(pyca)_2]$; in this complex both the nitrogen atom and the carboxylate oxygen atom of the acid ligand presumably co-ordinate to ruthenium to form a five-membered ring.

The last members of the series, *trans*-$[HL][RuO_2Cl_3L]$, were made as brown crystalline solids by reaction of RuO_4 with aqueous solutions of pyridine, 4-t-butylpyridine, 3-methyl-pyridine, or 3,4-dimethylpyridine containing HCl (Ru:L:Cl = 1:2:3). The pyridine complex has limited solubility in organic solvents; however the substituted pyridine analogues, especially 4Bu^t-py, are far more soluble.

(c) Vibrational Spectra and Structures of the Complexes.—It is likely that all the new complexes reported here contain 'ruthenyl' units, *i.e.* the *trans* O=Ru^{VI}=O moiety, since they display (Table 3) typically strong, sharp i.r. bands near 830 cm^{-1} corresponding to the asymmetric stretch $\nu_{asym.}(RuO_2)$ while the Raman spectra show a strong band near 850 cm^{-1} corresponding to the symmetric stretch $\nu_{sym.}(RuO_2)$. The centrosymmetric (or, for $[Ru_2O_6L_4]$, quasi-centrosymmetric) nature of this ruthenyl unit predicts that $\nu_{asym.}(RuO_2)$ be i.r. active but Raman inactive, and the reverse for $\nu_{sym.}(RuO_2)$. I.r. and Raman bands have been found in these regions for *trans*-$[RuO_2(NH_3)_4]Cl_2$,[17] *trans*-$[RuO_2(HIO_6)_2]^{6-}$,[2] *trans*-$[RuO_2(py)_4]^{2+}$, and *trans*-$[RuO_2Cl_2(py)_2]\cdot H_2O$.[1] For the $[Ru_2O_6L_4]$ species the presence of i.r. bands near 630 and 590 cm^{-1} may be associated with the Ru_2O_2 ring modes, as suggested for $[Ru_2O_6(py)_4]$[1] and for the corresponding ring modes of $[Os_2O_6(py)_4]$.[14] The strong i.r. bands near 330 cm^{-1} for complexes containing co-ordinated chloro ligands are likely to arise from $\nu_{asym.}(RuCl)$ stretches.

All the complexes show bands due to the co-ordinated ligand L; we list only the strong band near 1 000 cm^{-1} likely to arise from the two A_1 ring stretching modes[18] [ν(ring)] of the co-ordinated pyridine or substituted pyridine ligand (see Table 3).

Table 3. Analytical[a] and vibrational spectral data[b] for oxoruthenium(VI) complexes

Compound	Analysis (%)				v(ring)	$v_{asym.}(RuO_2)$ $[v_{sym.}(RuO_2)]$	$\delta(RuO_2)$	$v(Ru_2O_2)$ $[v(RuCl)]$
	C	H	N	Cl				
$[Ru_2O_6(py)_4]\cdot3.5H_2O$	35.8 (35.4)	2.9 (4.0)	8.3 (8.3)		1 040s	826s 815 (sh) [810m]	296w	635m 581m
$[Ru_2O_6(4Bu^t\text{-}py)_4]$	49.9 (51.5)	5.9 (6.2)	6.2 (6.7)		1 072s	815s [822m]	295w	547w
$[Ru_2O_6(bipy)_2]$	40.8 (39.3)	3.3 (2.6)	9.8 (9.2)		1 039s	810s	304w	577w
$[Ru_2O_6(Hnic)_4]\cdot4H_2O$	32.8 (33.4)	2.4 (3.3)	6.5 (6.5)		1 062s	843s	305w	600m
$[Ru_2O_6(Hpyca)_4]$	38.4 (36.4)	2.3 (2.6)	7.9 (7.1)		1 050s	833s 816m	318w	557w
$[Ru_2O_6(isna)_4]$	36.6 (36.6)	3.4 (3.1)	14.1 (14.2)		1 058s	825s	317w	obsc.
$[Ru_2O_6(bipy)_2]\cdot6H_2O$	33.6 (33.4)	3.5 (3.9)	7.9 (7.8)		1 038s	812s	313w	570m
trans-$[RuO_2(Hnic)_4][BF_4]_2\cdot2H_2O$	34.4 (34.5)	2.3 (2.9)	6.6 (6.7)		1 063s	841s [855s]	292w	—
trans-$[RuO_2(Hpyca)_4][BF_4]_2$	36.7 (36.3)	2.2 (2.0)	7.0 (7.0)		1 058s	837s	296w	—
trans-$[RuO_2(H_2pydca)_4][BF_4]_2\cdot2H_2O$	32.4 (33.2)	2.3 (2.4)	5.4 (5.5)		1 077s	852s	284w	—
trans-$[RuO_2Cl_2(4Bu^t\text{-}py)_2]\cdot H_2O$	44.5 (43.9)	5.5 (5.7)	5.8 (5.7)	15.6 (14.8)	1 065s	842s [858m]	263m	[327s]
trans-$[RuO_2Cl_2(4Cl\text{-}py)_2]$	28.2 (27.8)	1.9 (1.9)	6.6 (6.5)	31.6 (32.9)	1 052s	839s	284w	[335s]
trans-$[Hpy][RuO_2Cl_3(py)]$	32.3 (30.1)	2.4 (2.8)	7.6 (7.0)	25.4 (26.7)	1 068s	837s [833m]	289w	[327s]
trans-$[4Bu^t\text{-}Hpy][RuO_2Cl_3(4Bu^t\text{-}py)]$	42.3 (42.3)	5.3 (5.3)	5.5 (5.5)	20.2 (20.8)	1 074s	848s [840s]	277w	[308s]
trans-$[3Me\text{-}Hpy][RuO_2Cl_3(3Me\text{-}py)]$	33.9 (33.8)	3.3 (3.5)	6.5 (6.6)	24.6 (24.9)	1 084s	838s	278w	[311s]
trans-$[3,4Me_2\text{-}Hpy][RuO_2Cl_3(3,4Me_2\text{-}py)]$	36.7 (37.0)	4.1 (4.2)	6.1 (6.2)	22.8 (23.4)	1 093s	835s	285(sh)	[317s]

[a] Required values are given in parentheses. [b] s = Strong, m = medium, w = weak, sh = shoulder, and obsc. = obscured.

(*d*) *Reactions of* $[Ru_2O_6L_4]$ *and* trans-$[RuO_2Cl_nL_{4-n}]^{2-n}$.—Of the complexes considered here only $[Ru_2O_6(py)_4]\cdot3.5H_2O$, $[Ru_2O_6(4Bu^t\text{-}py)_4]$, trans-$[RuO_2Cl_2(4Bu^t\text{-}py)_2]\cdot H_2O$ and trans-$[4Bu^t\text{-}Hpy][RuO_2Cl_3(4Bu^t\text{-}py)]$ are sufficiently soluble in organic solvents to make detailed oxidation experiments worthwhile, though we have shown that all the complexes listed in Table 1 do function as oxidants towards alcohols. Since it is difficult to obtain substantial quantities of $[Ru_2O_6(4Bu^t\text{-}py)_4]$ or trans-$[RuO_2Cl_2(4Bu^t\text{-}py)_2]\cdot H_2O$, we have concentrated on $[Ru_2O_6(py)_4]\cdot3.5H_2O$, trans-$[RuO_2(py)_4][BF_4]_2\cdot H_2O$ and trans-$[4Bu^t\text{-}Hpy][RuO_2Cl_3(4Bu^t\text{-}py)]$ in CH_2Cl_2 or CH_3CN solutions as oxidants for alcohols. We have already shown that $[Ru_2O_6(py)_4]\cdot3.5H_2O$ and trans-$[RuO_2(py)_4]^{2+}$ function as overall four-electron oxidants, converting primary alcohols to aldehydes and secondary alcohols to ketones without competing olefinic double-bond cleavage under ambient conditions. Reactions may be rendered catalytic by using *N*-methylmorpholine *N*-oxide (mmo) as a co-oxidant. During preliminary work on this topic it became apparent that stoicheiometric oxidations of alcohols by $[Ru_2O_6(py)_4]\cdot3.5H_2O$ and trans-$[RuO_2(py)_4]^{2+}$ gave greater than 100% yields of product, based on the assumption that these were four-electron oxidants and that excess of substrate was used; aerobic co-oxidation was suspected, though oxidation in air of the substrates did not occur in the absence of the ruthenium complex under the conditions used. We have now established (Table 4) that there is modest aerobic co-oxidation. At 25 °C turnovers of the order of 12 are observed with $[Ru_2O_6(py)_4]\cdot3.5H_2O$ and of 10 with trans-$[4Bu^t\text{-}Hpy][RuO_2Cl_3(4Bu^t\text{-}py)]$ if oxygen is bubbled

through solutions of substrate and oxidant (under nitrogen the turnover is 2 for primary alcohols and 1 for secondary alcohols, as predicted on the assumption that these are four-electron oxidants, and in still air these values are increased). The use of acetonitrile rather than dichloromethane as solvent gives rise to higher turnovers, consistent with the greater solubility of dioxygen in CH_3CN, but the use of oxygen under pressure (2 or 5 atm) gave no increase in turnover. If a 10 mol % solution of copper(II) acetate is added to the solutions, a known procedure for enhancing aerobic co-oxidation,[19] there is little effect at room temperature but turnovers of up to 30 for primary and secondary alcohols are observed at 50 °C. With excess of mmo co-oxidant turnovers of up to 120 for primary alcohols and up to 80 for secondary alcohols are observed at 25 °C; in the presence of dioxygen these are increased to 140 and 100 respectively. Thus, for example, a solution of 5.08 g (37.86 mmol) of cinnamyl alcohol in acetonitrile is oxidised to 4.97 g (37.60 mmol; 99% conversion) of cinnamaldehyde by 0.183 g (0.27 mmol) of $[Ru_2O_6(py)_4]\cdot3.5H_2O$, a turnover of 14 at 25 °C over a 3-h period in the presence of dioxygen.

It is not clear how this aerobic oxidation occurs or why the turnovers are relatively low. We find that $[Ru_2O_6(py)_4]\cdot3.5H_2O$ reacts with dioxygen over a three hour period in acetonitrile to give a dark green insoluble material with analyses which approximate to an empirical formula $RuO_3\cdot py$, and which has strong i.r. bands at 825 and 940 cm^{-1} which could arise from a $v_{asym.}(RuO_2)$ stretch and the O–O stretch of a co-ordinated peroxo ligand respectively. Reactions of $[Ru_2O_6(py)_4]\cdot3.5H_2O$ with primary or secondary alcohols ROH give products with

Table 4. Typical catalytic oxidations by $[Ru_2O_6(py)_4] \cdot 3.5H_2O$ and $trans$-$[4Bu^t$-Hpy$][RuO_2Cl_3(4Bu^t$-py$)]$ [a]

Alcohol	Oxidant [b]	Product [c]	mmo co-oxidant [d]		O_2 co-oxidant [e]	
			Yield (%)	Turnover [f]	Yield (%)	Turnover [f]
Benzyl	(i)	A	99 [g]	120 [g]	96	10
	(ii)	A	92	38	93	8
p-Methoxybenzyl	(i)	A	99 [g]	120 [g]	94	12
	(ii)	A	97	54	92	10
Piperonyl	(i)	A	99 [g]	133 [g]	97	12
	(ii)	A	95	40	90	8
Cinnamyl	(i)	A	76 [g]	120 [g]	83	12
	(ii)	A	89	35	88	8
α-Tetralol [h]	(i)	K	94 [g]	70 [g]	95	8
	(ii)	K	93	49	92	7
Cyclohexanol	(i)	K	82 [g]	70 [g]		
	(ii)	K	86	18		
Geraniol	(i)	A	55 [g]	70 [g]		
	(ii)	A	46	21		

[a] All oxidations performed in CH_3CN at room temperature in the presence of powdered 4-Å molecular sieves over a period of 3 h. [b] (i) $[Ru_2O_6(py)_4] \cdot 3.5H_2O$; (ii) $trans$-$[4Bu^t$-Hpy$][RuO_2Cl_3(Bu^t$-py$)]$. [c] All yields quantified by preparation of the 2,4-dinitrophenylhydrazone derivative, A = corresponding aldehyde, K = corresponding ketone. [d] Three-fold excess of mmo. [e] Dioxygen passed through reaction solution. [f] Turnover = mol product/mol catalyst. [g] Reference 1. [h] 1,2,3,4-Tetrahydro-1-naphthenol.

variable analyses, i.r. spectra of which, however, show no bands due to R. Similar reactions with $trans$-$[4Bu^t$-Hpy$][RuO_2Cl_3$-$(4Bu^t$-py$)]$ give green solids whose analyses are close to the empirical formulation $[4Bu^t$-Hpy$][Ru_2OCl_7(4Bu^t$-py$)_3]$, whatever the nature of R. In no cases could crystals of these complexes be obtained for X-ray studies.

(e) Oxoruthenium(IV) Pyridine Complexes.—The complex $trans$-$[Ru(O)Cl(py)_4][ClO_4]$ has been reported; it is made by the reaction of $trans$-$[Ru(NO)Cl(py)_4][ClO_4]_2$ with ClO^-, and its X-ray crystal structure shows the Ru=O bond length to be quite long, at 1.862(8) Å.[20,21] It reacts with ROH (R = Me or Et) to give $[Ru^{III}(OR)Cl(py)_4]^+$,[22] but no other oxidations of alcohols were reported. We find that stoicheiometrically it functions as a two-electron oxidant with benzylic alcohols giving the respective aldehydes in moderate yield; with excess mmo or PhIO it oxidises primary alcohols to aldehydes and secondary alcohols to ketones with turnovers of up to 8 at room temperatures. A species analogous to this is likely to be an intermediate in the overall four-electron oxidation of alcohols by $trans$-$[RuO_2(py)_4]^{2+}$; however, attempts to isolate $trans$-$[Ru(O)Cl(py)_4]^+$ by reaction of $trans$-$[RuO_2(py)_4]^{2+}$ in HCl with 1 mole of a primary alcohol have failed, as have attempts to prepare it by oxidation of $trans$-$[RuCl_2(py)_4]$ by PhIO or mmo. Surprisingly, solutions of excess of mmo with $trans$-$[RuCl_2(py)_4]$ in CH_2Cl_2 or CH_3CN, or of excess of PhIO with $trans$-$[RuCl_2(py)_4]$ in benzene, did not oxidise alcohols.

Experimental

Hydrated ruthenium trichloride, $RuCl_3 \cdot nH_2O$, was supplied by Johnson-Matthey. This was converted into ruthenium dioxide, $RuO_2 \cdot nH_2O$, by heating under reflux in aqueous sodium hydroxide solution for 2 h. Ruthenium tetraoxide, RuO_4, was generated in gaseous form by a method based on that of Nakata.[23] Dried $RuO_2 \cdot nH_2O$ (0.75 g, ca. 5.5 mmol) was added to sodium periodate, $NaIO_4$ (2.5 g, 11.7 mmol) in water (20 cm³) and N_2 gas bubbled in to sweep out the RuO_4 vapour. We find,[4] as do other authors,[24] that the dioxide gives a better yield of RuO_4 than does the trichloride when used as starting material in this method.

Preparation and X-Ray Crystal Structure of $[Ru_2O_6(py)_4] \cdot$

$3.5H_2O$.—RuO_4, generated as above, was slowly passed into an ice-cold solution of pyridine (0.75 g, 9.5 mmol) in water (10 cm³) using N_2 gas. After 5 h the dark red-purple crystals formed were filtered off and placed immediately in a sealed specimen tube, in order to store them under the vapour pressure of their mother liquor and prevent their decomposition.

Crystal data. $C_{20}H_{27}N_4O_{9.5}Ru_2$, $M = 677.5$, triclinic, $a = 7.943(1)$, $b = 8.952(2)$, $c = 9.257(3)$ Å, $\alpha = 98.76(2)$, $\beta = 95.75(2)$, $\gamma = 98.08(1)°$, $U = 639$ Å³, space group $P\bar{1}$, $Z = 1$ (the molecule is disposed about a centre of symmetry), $D_c = 1.77$ g cm⁻³, $\mu(Cu-K_\alpha) = 103$ cm⁻¹, $\lambda = 1.541\,78$ Å, $F(000) = 339$.

Data collection and processing. As mentioned previously the crystals obtained were small, very unstable and of poor quality. The first crystal studied had decomposed by 50% by the time the lattice parameters had been determined. Consequently, in view of the very limited supply of suitable crystals, data were collected to only low resolutions at high speed. Total set-up and data collection time was 6 h. Nicolet R3m diffractometer, ω-scan method ($2\theta \leqslant 90°$), graphite-monochromated $Cu-K_\alpha$ radiation; 1 145 independent measured reflections, 1 094 observed $[|F_o| > 3\sigma(|F_o|)]$, corrected for Lorentz and polarisation factors; numerical absorption correction (face indexed crystal), maximum and minimum transmission factors 0.705 and 0.401.

Structure analysis and refinement. The structure was solved by the heavy-atom method. The non-hydrogen atoms were refined anisotropically. The positions of the water protons were not located. The positions of the remaining hydrogen atoms were idealised, C–H 0.96 Å, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. The pyridine rings were refined as idealised rigid bodies. Refinement was by block-cascade, full-matrix least squares to give R 0.065, R' 0.073 $[w^{-1} = \sigma^2(F) + 0.000\,30F^2]$. The maximum and minimum residual electron densities in the final ΔF map were 0.84 and -0.86 e Å⁻³ respectively. The mean and maximum shifts/error in the final refinement cycle were 0.000 and 0.002 respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[25]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Preparation of Remaining Complexes.—[Ru$_2$O$_6$L$_4$] (L = 4Bu^t-py *or* $\frac{1}{2}$bipy). The compound RuO$_4$ [generated as above from RuO$_2$·nH$_2$O (0.75 g), NaIO$_4$ (2.5 g) and water (20 cm^3)] was passed into a solution of 4-t-butylpyridine (0.85 g, 6.3 mmol) in CCl$_4$ (Analar grade, 15 cm^3) at 0 °C. After 5 h, passage of RuO$_4$ was ceased and the red-brown solution was stored at 5 °C for 72 h, after which time a dark red precipitate of [Ru$_2$O$_6$(4Bu^t-py)$_4$] had formed. The solid was filtered off, washed with diethyl ether, and air-dried. Similarly, the complex [Ru$_2$O$_6$(bipy)$_2$] was prepared as a red-brown precipitate by passing RuO$_4$ into an ice-cold solution of 2,2′-bipyridyl (1.0 g, 6.4 mmol) in CCl$_4$ (10 cm^3) for 3 h.

[Ru$_2$O$_6$L$_4$]·nH$_2$O (L = Hnic, Hpyca, isna, *or* $\frac{1}{2}$bipy). The preparation of [Ru$_2$O$_6$(Hnic)$_4$]·4H$_2$O was typical. The compound RuO$_4$, generated as above, was passed into an ice-cold solution of isonicotinamide (1.42 g, 11.5 mmol) in water (15 cm^3). The solution turned brown-green, and after 5 h precipitation of a brown-green solid was complete. This was filtered off, washed with cold water (2 × 10 cm^3), and dried *in vacuo* over silica gel.

trans-[RuO$_2$L$_4$][BF$_4$]$_2$·nH$_2$O (L = Hpyca, Hnic, *or* H$_2$-pydca). The preparation of *trans*-[RuO$_2$(Hpyca)$_4$][BF$_4$]$_2$ was typical. The compound RuO$_4$ was generated and passed into CCl$_4$ (150 cm^3); the resulting solution was stirred vigorously with 1 mol dm^{-3} NaOH overnight to give a red-brown aqueous solution containing sodium ruthenate(VI) (*ca.* 2.3 mmol ruthenium per 10 cm^3). To 10 cm^3 of the ruthenate solution were added NaOH (0.1 g) and Hpyca (1.13 g, 9.2 mmol) with stirring. After 10 min the solution was cooled to 0 °C and treated with HBF$_4$–water (1:1) dropwise until a yellow-brown precipitate ceased to form. The solid was filtered off, washed with the minimum of cold water and diethyl ether, and dried *in vacuo*.

trans-[RuO$_2$Cl$_2$(4Bu^t-py)$_2$]·H$_2$O. To a solution of t-butyl-pyridine (0.93 g, 6.9 mmol) in 10.6 mol dm^{-3} HCl (1.40 cm^3, *ca.* 15 mmol) at 0 °C was added basic sodium ruthenate solution (prepared as above) (10 cm^3) with stirring. A yellow-green solid was precipitated, filtered off, washed with cold water, and dried *in vacuo* over silica gel.

trans-[RuO$_2$Cl$_2$(4Cl-py)$_2$]. The compound RuO$_4$, generated as above, was passed into an ice-cold solution of 4-chloro-pyridine hydrochloride (0.80 g, 5.33 mmol) in water (10 cm^3). After 2.5 h, precipitation of a yellow-green solid was complete; this was filtered off, washed with cold water, and dried *in vacuo* over silica gel.

trans-[HL][RuO$_2$Cl$_3$L] (L = py, 4Bu^t-py, 3Me-py, *or* 3,4Me$_2$-py). The preparation of *trans*-[4Bu^t-Hpy][RuO$_2$Cl$_3$-(4Bu^t-py)] was typical. The compound RuO$_4$ was generated as above and passed into a solution of 4-t-butylpyridine (1.55 g, 11.5 mmol) in water (8 cm^3) and 10.6 mol dm^{-3} HCl (3 cm^3, *ca.* 30 mmol) at 0 °C. The use of a slight excess of HCl was required to prevent formation of the *trans*-[RuO$_2$Cl$_2$(4Bu^t-py)$_2$] species. After 4 h the solution was brown and passage of RuO$_4$ was ceased. On standing at room temperature overnight brown crystals appeared. These were filtered off, washed with the minimum of cold water, and dried *in vacuo* over silica gel.

Oxidations.—(*a*) *Stoicheiometric.* All of the complexes reported here function as stoicheiometric oxidants towards alcohols, though only those with appreciable solubility in organic solvents were studied in detail. The procedure for the stoicheiometric oxidation of *p*-methoxybenzyl alcohol by *trans*-[4Bu^t-Hpy][RuO$_2$Cl$_3$(4Bu^t-py)] was typical. To a solution of *p*-methoxybenzyl alcohol (69.1 mg, 0.5 mmol) in CH$_3$CN (5 cm^3) containing powdered 4-Å molecular sieves (0.25 g, activated by heating prior to use) was added *trans*-[4Bu^t-pyH][RuO$_2$Cl$_3$(4Bu^t-py)] (127.7 mg, 0.25 mmol). The reaction mixture was stirred at room temperature under N$_2$ for 3 h,

diluted with CH$_3$CN, filtered to remove the sieves, and evaporated to dryness. The residue was dissolved in CH$_2$Cl$_2$ (25 cm^3) and the solution washed with 1 mol dm^{-3} sodium thiosulphate solution (to remove ruthenium from the organic layer) and water (25 cm^3). The CH$_2$Cl$_2$ solution was dried over anhydrous MgSO$_4$, filtered, and evaporated to dryness to yield the product, *p*-methoxybenzaldehyde, which was quantified as its 2,4-dinitrophenylhydrazone derivative.

(*b*) *Catalytic* (N-*methylmorpholine*-N-*oxide as co-oxidant*). The catalytic oxidation of piperonyl alcohol by *trans*-[4Bu^t-Hpy][RuO$_2$Cl$_3$(4Bu^t-py)] was typical. To a solution of piper-onyl alcohol (114.1 mg, 0.75 mmol) in CH$_3$CN (10 cm^3) were added powdered 4-Å molecular sieves (0.25 g), mmo (263.6 mg, 2.25 mmol), and *trans*-[4Bu^t-Hpy][RuO$_2$Cl$_3$(4Bu^t-py)] (9.1 mg, 1.78 × 10^{-2} mmol). The reaction mixture was stirred at room temperature for 3 h, then diluted with CH$_3$CN, filtered, and evaporated to dryness. The residue was dissolved in CH$_2$Cl$_2$ (25 cm^3) and the resulting solution washed with 1 mol dm^{-3} sodium thiosulphate solution (25 cm^3), water, saturated copper sulphate solution (25 cm^3, to remove the mmo and its products), and water again. The organic extract was dried over anhydrous MgSO$_4$, filtered, and evaporated to dryness to yield the product piperonal, which was quantified as its 2,4-dinitrophenyl-hydrazone derivative. A yield of 95% piperonal was produced, corresponding to a turnover of 40.

(*c*) *Aerobically assisted oxidations* (*molecular oxygen as co-oxidant*). The oxidation of *p*-methoxybenzyl alcohol by [Ru$_2$O$_6$(py)$_4$]·3.5H$_2$O in the presence of O$_2$ was typical. Dioxygen was bubbled through a solution of *p*-methoxybenzyl alcohol (41.5 mg, 0.3 mmol) and [Ru$_2$O$_6$(py)$_4$]·3.5H$_2$O (16.9 mg, 2.5 × 10^{-2} mmol) in CH$_3$CN (10 cm^3) for 3 h in the presence of powdered molecular sieves. The solution was treated as above for the stoicheiometric oxidation, and 95% of *p*-methoxybenzaldehyde was produced, corresponding to a turnover of 12. A similar oxidation conducted under reflux at 50 °C gave no appreciable increase in turnover, nor did oxidations performed under O$_2$ pressures of up to 5 atm in a pressure bottle. Addition of 10 mol % copper(II) acetate to the reaction solution gave no increase in turnover at room temperature, but increased turnover to 28 at 50 °C. The highest turnovers (up to 140 for *p*-methoxybenzyl alcohol) were achieved by bubbling O$_2$ through a catalytic mmo oxidation in CH$_3$CN at room temperature.

Preparation of trans-[Ru(O)Cl(py)$_4$]A (A = ClO$_4$ *or* PF$_6$). —The complexes *trans*-[Ru(NO)Cl(py)$_4$]A$_2$ (A = ClO$_4$ or PF$_6$) were prepared by the method of Bottomley and Mukaida.[26] The corresponding mono-oxo salts were prepared by reaction of aqueous *trans*-[Ru(NO)Cl(py)$_4$]A$_2$ with commercial sodium hypochlorite solution (available chlorine *ca.* 8%) over a period of 24 h in a method based on that of Mukaida and co-workers.[21]

Stoicheiometric and Catalytic Oxidations using trans-[Ru(O)Cl(py)$_4$][ClO$_4$].—The oxidations of benzyl alcohol were typical.

(*i*) *Stoicheiometric.* To a solution of benzyl alcohol (1.1 mg, 0.10 mmol) in CH$_3$CN (5 cm^3) was added *trans*-[Ru(O)Cl-(py)$_4$][ClO$_4$] (5.7 mg, 0.10 mmol). The solution was stirred in the presence of molecular sieves for 3 h, and worked up in the manner described above. The yield of benzaldehyde was 45%.

(*ii*) *Catalytic.* A solution of *trans*-[Ru(O)Cl(py)$_4$][ClO$_4$] (10.7 mg, 1.9 × 10^{-2} mmol) and mmo (134 mg, 1.14 mmol) in CH$_3$CN (10 cm^3) was added to benzyl alcohol (41 mg, 0.38 mmol) and the solution stirred in the presence of powdered molecular sieves for 3 h. The reaction was worked up as above, and the yield of 40% benzaldehyde produced corresponds to a turnover of 8.

Carbon, chlorine, hydrogen, and nitrogen analyses were carried out by the Microanalytical Department of Imperial College. Raman spectra were run on pressed discs with KBr supports on a Spex Ramalog 5 instrument with krypton ion (6 471 and 5 682 Å) and argon-ion (5 145 Å) laser excitation. I.r. spectra were recorded on Perkin-Elmer 683(IR) and 1720 (FTIR) instruments as liquid paraffin mulls between potassium bromide or caesium iodide plates. In all oxidation experiments 2,4-dinitrophenylhydrazone derivatives were prepared using a saturated methanolic solution of 2,4-dinitrophenylhydrazine (acidified with sulphuric acid) and were compared with authentic samples.

Acknowledgements

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