DALTON
FULL PAPER

Ozonolysis for the preparation of high oxidation-state transition-metal complexes and the crystal structure of $[\mathrm{PPh_4}]_2[\mathrm{Ru_2O(\mu\text{-}OCOEt)_2Cl_6}]$ †

Alan J. Bailey, William P. Griffith,* Stephen P. Marsden, Andrew J. P. White and David J. Williams *

Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY

Received 3rd August 1998, Accepted 7th September 1998

An ozone–oxygen mixture has been used to generate a number of high oxidation-state transition-metal complexes in aqueous solution at room temperature by simple and safe procedures. Species so prepared include the oxo species $[\mathrm{Os^{VIII}O_4}]$, $[\mathrm{Ru^{VIII}O_4}]$, *cis*-$[\mathrm{Os^{VIII}O_4(OH)_2}]^{2-}$, *trans*-$[\mathrm{Os^{VI}O_2(OH)_4}]^{2-}$, $[\mathrm{Ru^{VII}O_4}]^-$, *trans*-$[\mathrm{Ru^{VI}(OH)_2O_3}]^{2-}$, $[\mathrm{V^VO_4}]^{3-}$ and the new complex $[\mathrm{PPh_4}]_2[\mathrm{Ru_2O(\mu\text{-}OCOEt)_2Cl_6}]$ **1** for which the crystal structure is reported; the polyoxometalates $\mathrm{K_6[Mn^{IV}Mo_9O_{32}]\cdot10H_2O}$, $\mathrm{K_8[Mn^{IV}W_6O_{24}]\cdot6H_2O}$, $\mathrm{[NH_4]_2[Mn^{IV}Mo_6H_6O_{24}]\cdot20H_2O}$ and $\mathrm{Na_8[Ce^{IV}W_{10}O_{36}]\cdot8H_2O}$; the chloro complexes $[\mathrm{M^{IV}Cl_6}]^{2-}$ (M = Pt, Pd, Ir) and $[\mathrm{Au^{III}Cl_4}]^-$, and manganic acetate $[\mathrm{Mn^{III}(OAc)_3}]\cdot2\mathrm{H_2O}$. Ozonolytic oxidation of coordinated benzylamine in *cis*-$[\mathrm{Ru^{II}(bipy)_2(NH_2CH_2Ph)_2}][\mathrm{PF_6}]_2$ to coordinated benzonitrile in *cis*-$[\mathrm{Ru^{II}(bipy)_2(NCPh)_2}][\mathrm{PF_6}]_2$ is also reported.

We have long been interested in the preparation, characterisation and application of high oxidation-state transition-metal complexes as catalysts for selective organic oxidations.[1–5] A number of methods have been described in the literature for the preparation of such species, but many are difficult or time-consuming. Here we show that an ozone–oxygen ($\mathrm{O_3–O_2}$) gas mixture (typically 0.02 g of $\mathrm{O_3}$ in 2 $\mathrm{dm^3}$ of $\mathrm{O_2}$ per min), generated by a normal commercial ozoniser, is capable of producing a number of such complexes by simple, safe and environmentally acceptable procedures, in aqueous solution under ambient conditions, with dioxygen as the only significant side-product.

To our knowledge there has been no extended study prior to this work on the use of ozone to prepare transition-metal complexes in high oxidation states. Ozonolysis has been used to prepare some silver(II) complexes, *e.g.* $[\mathrm{Ag^{II}(NO_3)_2(bipy)}]$ from $[\mathrm{Ag(NO_3)(bipy)_2}]$[6] and platinum(IV) species, *e.g.* $\mathrm{K_2[Pt^{IV}Cl_6]}$ from $\mathrm{K_2[PtCl_4]}$.[7] Recently the complexes $\mathrm{LiM^I[M^{III}IO_6]}$ ($\mathrm{M^I}$ = K, Rb, Cs; $\mathrm{M^{III}}$ = Fe, Co) have been isolated using ozonolysis.[8] An unspecified nickel(IV) periodato complex has been made using this technique,[9] and Kiselev *et al.* have found that ozonolysis of $[\mathrm{Pt(OH)_6}]^{2-}$ in aqueous base gives ill-defined superoxo complexes.[10]

Throughout the reactions described below the use of oxygen alone rather than an $\mathrm{O_3–O_2}$ mixture did not give the product reported.

Results and discussion

(a) Ozonolytic preparation of oxo complexes; the crystal structure of $[\mathrm{PPh_4}]_2[\mathrm{Ru_2O(\mu\text{-}OCOEt)_2Cl_6}]$

(i) Syntheses. Preparation of the three well-established oxidants[3,5] $[\mathrm{Ru^{VIII}O_4}]$, $[\mathrm{Ru^{VII}O_4}]^-$ and *trans*-$[\mathrm{Ru^{VI}(OH)_2O_3}]^{2-}$ was achieved by ozonolysis of aqueous solutions of $\mathrm{RuCl_3}\cdot n\mathrm{H_2O}$ (or suspensions of $\mathrm{RuO_2}\cdot n\mathrm{H_2O}$) in water at pH 7 for $[\mathrm{Ru^{VIII}O_4}]$, in aqueous borax buffer ($\mathrm{Na_2B_4O_7\cdot10H_2O}$) at pH 10.3 for $[\mathrm{Ru^{VII}O_4}]^-$ and in molar aqueous KOH for *trans*-$[\mathrm{Ru^{VI}(OH)_2O_3}]^{2-}$. The use of $\mathrm{O_3–O_2}$ rather than the more commonly used oxidants[5] such as $\mathrm{IO_4}^-$, ClO^-, $\mathrm{BrO_3}^-$ or $\mathrm{S_2O_8}^{2-}$ avoided contamination of the products by materials such as $\mathrm{IO_3}^-$ *etc.*: the ozonolytic preparations are simple and clean, leaving no side-products. In general for these oxoruthenates ozonolysis was faster for $\mathrm{RuCl_3}\cdot n\mathrm{H_2O}$ (*ca.* 15 min) than for $\mathrm{RuO_2}\cdot n\mathrm{H_2O}$ (*ca.* 35 min) presumably due to the solubility of the former. The three oxoruthenates so produced were identified from their distinctive electronic spectra.[5,11]

Two osmium(VIII) species $[\mathrm{OsO_4}]$ and $[\mathrm{OsO_4(OH)_2}]^{2-}$ were also isolated from the oxidation of the osmium(VI) species $[\mathrm{OsO_2(OH)_4}]^{2-}$ by $\mathrm{O_3–O_2}$ in solutions of pH 7 and 13, respectively. They were identified by their respective electronic spectra.[1,12] Similarly, orthovanadate $[\mathrm{V^VO_4}]^{3-}$ was made by ozonolysis of vanadyl sulfate, $\mathrm{V^{IV}O(SO_4)}\cdot n\mathrm{H_2O}$, in aqueous base and identified by its known[13] electronic spectrum.

In earlier work we reported the isolation of salts of the carboxylato complexes *cis*-$[\mathrm{Ru^{VI}O_2(OCOR)Cl_2}]^-$ (R = Me, Et, Pr, $\mathrm{CH_2F}$) by reaction of $[\mathrm{RuO_4}]$ with concentrated $\mathrm{RCO_2H}$ in the presence of $(\mathrm{PPh_4})\mathrm{Cl}$.[14] In an attempt to prepare these species by ozonolytic procedures we passed an $\mathrm{O_3–O_2}$ mixture through a solution of $\mathrm{RuCl_3}\cdot n\mathrm{H_2O}$ in $\mathrm{RCO_2H}$ and obtained products which we were unable to characterise, except for the reaction in propionic acid. This gave orange-red crystals, which were found from a single crystal X-ray study to be the new complex $[\mathrm{PPh_4}]_2[\mathrm{Ru_2O(\mu\text{-}OCOEt)_2Cl_6}]$ **1** (see below). "Lantern"-type dinuclear carboxylates such as $[\mathrm{Ru_2(\mu\text{-}OCOR)_4Cl}]$ (R = Me, Et, Pr) have long been known[15] but to our knowledge there are no examples in the literature of a dinuclear complex of ruthenium containing both μ-oxo and μ-carboxylato ligands. There are crystal structures of $[\mathrm{L_2Ru^{III}{}_2O(\mu\text{-}OAc)_2}][\mathrm{PF_6}]_2$ (L = *N*,*N′*,*N″*-trimethyl-1,4,7-triazacyclononane)[16] and of $[\mathrm{Ru^{III}{}_2O(\mu\text{-}OAc)_2(bipy)_2(mim)_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O\cdot MeOH}$ (mim = 1-methylimidazole),[17] but **1** is the first example of a tetravalent ruthenium complex containing both a bridging oxo ligand and two bridging carboxylate groups.

(ii) The crystal structure of 1. The X-ray analysis revealed the product to be the novel, oxo-bridged, dimeric complex depicted in Fig. 1. The crystals contain two crystallographically

---

† Studies on transition-metal nitrido and oxo complexes. Part 19.[1]

Table 1 Selected bond lengths (Å) and angles (°) for **1**

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Ru(1)–O(1)	1.777(7)	1.799(7)	Ru(1)–O(2)	2.070(9)	2.067(8)
Ru(1)–O(4)	2.070(8)	2.087(8)	Ru(1)–Cl(1)	2.318(3)	2.322(3)
Ru(1)–Cl(2)	2.301(3)	2.296(3)	Ru(1)–Cl(3)	2.312(3)	2.318(3)
Ru(2)–O(1)	1.790(8)	1.787(7)	Ru(2)–O(3)	2.087(8)	2.068(7)
Ru(2)–O(5)	2.076(10)	2.080(8)	Ru(2)–Cl(4)	2.311(4)	2.318(3)
Ru(2)–Cl(5)	2.314(4)	2.321(3)	Ru(2)–Cl(6)	2.303(4)	2.325(3)
O(1)–Ru(1)–O(2)	86.5(3)	87.2(3)	O(1)–Ru(1)–O(4)	88.4(3)	87.7(3)
O(2)–Ru(1)–O(4)	91.4(4)	91.3(3)	O(1)–Ru(1)–Cl(2)	168.1(3)	168.6(2)
O(2)–Ru(1)–Cl(2)	84.9(3)	85.1(2)	O(4)–Ru(1)–Cl(2)	83.6(2)	84.1(2)
O(1)–Ru(1)–Cl(3)	97.3(3)	95.8(2)	O(2)–Ru(1)–Cl(3)	89.6(3)	88.7(3)
O(4)–Ru(1)–Cl(3)	174.2(3)	176.5(2)	Cl(2)–Ru(1)–Cl(3)	90.8(1)	92.4(1)
O(1)–Ru(1)–Cl(1)	95.3(3)	96.1(2)	O(2)–Ru(1)–Cl(1)	178.2(3)	176.6(2)
O(4)–Ru(1)–Cl(1)	88.2(3)	88.0(2)	Cl(2)–Ru(1)–Cl(1)	93.3(1)	91.5(1)
Cl(3)–Ru(1)–Cl(1)	90.6(1)	91.8(1)	O(1)–Ru(2)–O(5)	86.5(4)	86.0(3)
O(1)–Ru(2)–O(3)	88.1(3)	87.9(3)	O(5)–Ru(2)–O(3)	91.6(4)	90.9(3)
O(1)–Ru(2)–Cl(6)	94.9(3)	95.0(2)	O(5)–Ru(2)–Cl(6)	89.4(3)	89.7(2)
O(3)–Ru(2)–Cl(6)	176.9(3)	177.0(2)	O(1)–Ru(2)–Cl(4)	96.4(3)	96.8(3)
O(5)–Ru(2)–Cl(4)	177.1(3)	176.5(3)	O(3)–Ru(2)–Cl(4)	88.3(3)	87.1(2)
Cl(6)–Ru(2)–Cl(4)	90.6(2)	92.1(1)	O(1)–Ru(2)–Cl(5)	168.5(3)	168.1(2)
O(5)–Ru(2)–Cl(5)	84.8(3)	84.6(3)	O(3)–Ru(2)–Cl(5)	84.8(3)	84.9(2)
Cl(6)–Ru(2)–Cl(5)	92.4(1)	92.3(1)	Cl(4)–Ru(2)–Cl(5)	92.3(2)	92.3(1)
Ru(1)–O(1)–Ru(2)	139.2(4)	138.3(4)	C(1)–O(2)–Ru(1)	129.7(9)	125.9(7)
Cl(1)–O(3)–Ru(2)	129.3(8)	129.6(7)	C(4)–O(4)–Ru(1)	130.3(9)	129.6(7)
C(4)–O(5)–Ru(2)	128.1(8)	127.9(7)			

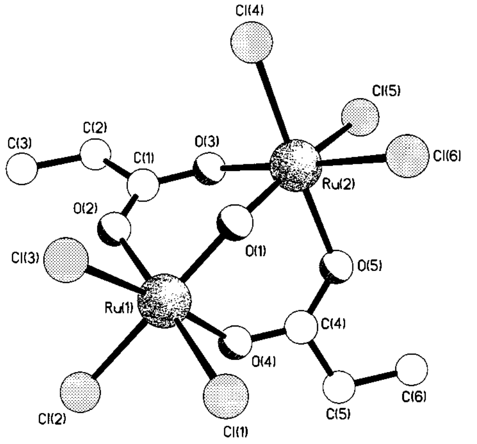

Fig. 1 One of the pair of crystallographically independent anions present in the structure of **1**. The non-bonded Ru $\cdots$ Ru separations are 3.34 Å (molecule 1) and 3.35 Å (molecule 2).

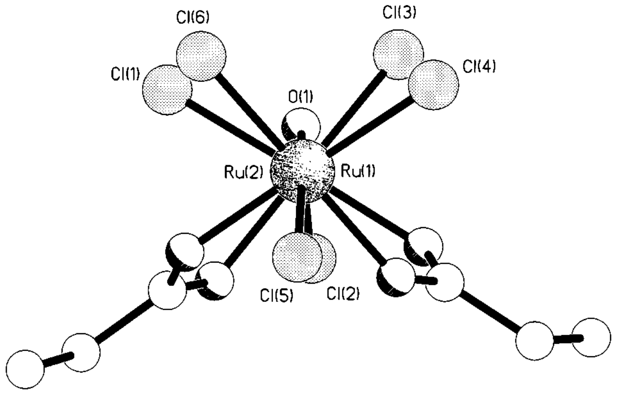

Fig. 2 View down the Ru $\cdots$ Ru vector of the anions in **1** showing the "λ–λ" twisting of the planes of the two acid groups and the non-eclipsing of the chloride substituents.

independent molecules of essentially identical conformations [the best fit of all the non-hydrogen atoms with the exception of the terminal methyl groups has an r.m.s. deviation of only 0.069 Å] each possessing molecular C_2 symmetry about an axis bisecting the Ru–O–Ru angle. The geometry at each of the four independent ruthenium centres is slightly distorted octahedral with angles in the ranges 83.6(2) to 97.3(3)° and 168.1(3) to 178.2(3)°, the largest distortions in the *trans* angles in each case being associated with the bridging oxo ligand. There is a characteristic but small displacement of *ca.* 0.06 Å of each ruthenium atom out of the equatorial plane towards the bridging oxo ligand. The Ru–Cl distances (Table 1) do not differ markedly, ranging between 2.296(3) and 2.325(3) Å, there being no noticeable *trans* influence due to the bridging oxo ligand. As expected the Ru–O distances fall into two distinct groups with those to the bridging oxo ligand being significantly shorter [1.777(7) to 1.799(7) Å] than those to the acids [2.067(8) to 2.087(8) Å]. Each molecule has a distinctive propeller-like conformation with the plane of each O_2CC unit being noticeably inclined to the Ru $\cdots$ Ru vector, the two six-membered pseudo-chelate rings in each molecule having the same configuration (Fig. 2).

The only cation $\cdots$ anion interactions of note are a pair of C–H $\cdots$ Cl hydrogen bonds between one of the cationic phenyl ring protons and Cl(1) in one anion, and from a different phenyl proton to Cl(3′) in another; the C $\cdots$ Cl, H $\cdots$ Cl distances and C–H $\cdots$ Cl angles are 3.66, 2.73 Å, 164° and 3.66, 2.70 Å, 174° respectively.

(b) Synthesis of high oxidation state metal centres in polyoxometalates

The synthesis of high oxidation state metal centres in polyoxometalates is an area of current interest.[18] Many polyoxometalates mimic porphyrin oxidation catalysts in that they are robust, but are much simpler and cheaper to make than porphyrin complexes (thus $[(WZnMn_2^{II})(ZnW_9O_{34})_2]^{12-}$ has recently been shown to be an active epoxidation catalyst with H_2O_2 as co-oxidant[19]). We describe here the preparations of four typical polyoxometalates containing hetero-atoms in high oxidation states, which are difficult or tedious to isolate by conventional methods, but which are easily obtained by ozonolysis.

The normal preparation of $K_6[Mn^{IV}Mo_9O_{32}]\cdot 10H_2O$ involves heating manganese sulfate, sodium molybdate and oxone ($2KHSO_5\cdot KHSO_4\cdot K_2SO_4$) to 40 °C in an acetic acid–KOH buffer for 4 h;[20] however we found this method to be difficult, yielding products of varying purities. However, if an O_3–O_2 mixture is passed through a $MnSO_4$–$[MoO_4]^{2-}$ solution at pH

4.5, thus replacing oxone as the oxidant, the reaction is complete within 45 min without heating. Deep red crystals of $K_6[Mn^{IV}Mo_9O_{32}]\cdot10H_2O$ were formed and characterised by ICP analysis, electronic and IR spectroscopies. This is a considerable improvement over the method previously reported[20] since it avoids the use of heat and is much faster. When $Na_2[WO_4]$ was used in place of $Na_2[MoO_4]$ a different type of polyoxometalate, $K_8[Mn^{IV}W_6O_{24}]\cdot6H_2O$, was isolated on ozonolysis and identified by measurement of its known[21] unit cell dimensions. The complex is normally prepared by prolonged reaction of $Na_2[WO_4]$, $MnSO_4$ and hot aqueous $K_2S_2O_8$;[21] again the ozonolytic reaction is much cleaner and occurs at room temperature. Reaction of the species formulated as $[NH_4]_4[Mn^{II}Mo_6H_6O_{24}]\cdot5H_2O$[22] with O_3–O_2 gave a new complex which analysed as $[NH_4]_2[Mn^{IV}Mo_6H_6O_{24}]\cdot20H_2O$. It is not clear what the structure of this or the precursor complex is but presumably it has an Anderson-type structure, as has $K_8[Mn^{IV}W_6O_{24}]\cdot6H_2O$.[21] The known[23] lanthanopolyoxometalate $K_8[Ce^{IV}W_{10}O_{36}]\cdot8H_2O$ was similarly made in good yield by ozonolysis of an aqueous HCl solution (pH 2) of $K_9[Ce^{III}W_{10}O_{36}]\cdot6H_2O$.

(c) Preparation of other high-oxidation state complexes

Ozonolysis of $PdCl_2$ in aqueous HCl (pH 2) followed by addition of excess tetrabutylammonium chloride gave a red precipitate of $[^nBu_4N]_2[PdCl_6]$; the normal method uses chlorine in place of ozone.[24] Similarly, ozonolysis of $[PtCl_4]^{2-}$ in aqueous HCl (pH 2) followed by addition of tetrabutylammonium chloride gave the yellow $[^nBu_4N]_2[Pt^{IV}Cl_6]$. Ozonolysis of $[IrCl_6]^{3-}$ in a similar HCl solution gave the black precipitate $[^nBu_4N]_2[Ir^{IV}Cl_6]$; again a conventional preparation[25] would have involved chlorination of $[IrCl_6]^{3-}$. Unfortunately, although ozonolysis of $[Os^{IV}Cl_6]^{2-}$ in HCl caused a change in colour of the solution from orange to yellow and the addition of tetraphenylphosphonium chloride gave a yellow precipitate, the product could not be identified; it was neither the known $[PPh_4][Os^{V}Cl_6]$[26] nor $[PPh_4]_4[Os^{IV}_2OCl_{10}]$.[27] Reaction[28] of $[Au^{I}Cl_2]^-$ with O_3–O_2 in HCl gave the bright yellow $[Au^{III}Cl_4]^-$.

Manganese(III) acetate, $[Mn(OAc)_3]\cdot2H_2O$, is normally made by reaction of $Mn(OAc)_2$ with permanganate[29] or by anodic oxidation,[30] and may have the μ_3-oxo bridged structure, $[Mn_3O(OAc)_6(OAc)(AcOH)]_n\cdot xH_2O$.[31] We find that O_3–O_2 with manganese(II) acetate in glacial acetic acid yields a dark brown product which analyses as $Mn(OAc)_3\cdot2H_2O$.

The oxidation of $[Fe^{II}(CN)_6]^{4-}$ to $[Fe^{III}(CN)_6]^{3-}$ and the oxidation of Fe(II) to Fe(III) salts in neutral aqueous solution was quickly effected by ozonolysis. Although these oxidations occurred when O_2 alone was passed through the solutions, the rates at which the transformations were complete were much greater when O_3–O_2 was used.

(d) Oxidation of coordinated ligands

An unusual case of amine dehydrogenation effected by ozone occurred when the red *cis*-$[Ru^{II}(bipy)_2(NH_2CH_2C_6H_5)_2][PF_6]_2$ in CH_2Cl_2 was treated with O_3–O_2 for 10 min; the yellow *cis*-$[Ru^{II}(bipy)_2(NCC_6H_5)_2][PF_6]_2\cdot3H_2O$ was formed, dehydrogenation of the coordinated amine ligands to coordinated nitrile having occurred. We have recently shown that peroxodisulfate will also effect this reaction, though over a 3 h period and at elevated temperatures,[1] and this transformation has also been accomplished electrochemically and with cerium(IV).[32]

Conclusions

We have shown that an O_3–O_2 mixture effects useful inorganic oxidations. It is worth noting that in a number of cases such oxidations can also be accomplished, albeit as we have shown less effectively, by peroxodisulfate (*e.g.* preparation of some silver(II) complexes,[6] $[RuO_4]^-$ and *trans*-$[Ru(OH)_2O_3]^{2-}$,[5] *cis*-$[OsO_4(OH)_2]^{2-}$,[2] $K_8[Mn^{IV}W_6O_{24}]\cdot6H_2O$[21] and *cis*-$[Ru^{II}(bipy)_2(NCC_6H_5)_2][PF_6]_2$[1]). This is understandable since the oxidation potential of ozone (+2.07 V) and that of peroxodisulfate (+2.01 V)[33] are very close.

Experimental

General

Sodium molybdate and tungstate, vanadyl sulfate, cerium(III) chloride and manganese(II) acetate were purchased from Aldrich and used without further purification; $RuCl_3\cdot nH_2O$, OsO_4, $Na_2[OsCl_6]\cdot nH_2O$ and $Na_2[IrCl_6]\cdot nH_2O$ were supplied by Johnson, Matthey and used without purification.

General oxidation procedures

The reactant metal complex was dissolved in water and O_3–O_2 (0.02 g of O_3 in 2 dm^3 of O_2 per min) was bubbled through the solution for 30 min or until a significant colour change was observed. In general reactions were carried out with small quantities of reactant, but the reactions may be scaled up without problems arising; we have shown this to be the case for $[^nBu_4N]_2[Pd^{IV}Cl_6]$.

The ozoniser was a Model TOG A1 Tri-Ox ozoniser; the ozone content was determined for various oxygen gas flows and applied potentials by titration against thiosulfate solution of the iodine released by ozone from standard iodide solution.[34]

(a) Preparation of oxo complexes

$[Ru^{VIII}O_4]$. $RuCl_3\cdot3H_2O$ (0.026 g, 0.1 mmol) or $RuO_2\cdot3H_2O$ (0.16 g, 0.1 mmol) was dissolved in water (50 cm^3, pH 7) and O_3–O_2 was bubbled through for 30 min until a bright yellow coloured solution was observed. The species was identified from its electronic spectrum (λ_{max}/nm: 385, 311) corresponding to that previously reported.[11]

$[Ru^{VII}O_4]^-$. $RuCl_3\cdot nH_2O$ (0.026 g, 0.1 mmol) was dissolved in a borax buffer (50 cm^3, pH 10.3; curiously the use of a carbonate–bicarbonate buffer at the same pH gave only RuO_2). The O_3–O_2 mixture was bubbled through for 30 min until a dark green coloured solution was observed. A suspension of $RuO_2\cdot nH_2O$ (0.16 g, 0.1 mmol) may also be used but the reaction is slower. The perruthenate ion was identified from its electronic spectrum (λ_{max}/nm: 382, 317) corresponding to that previously reported.[5,11]

***trans*-$[Ru^{VI}(OH)_2O_3]^{2-}$.** $RuCl_3\cdot3H_2O$ (0.026 g, 0.1 mmol) or $RuO_2\cdot3H_2O$ (0.16 g, 0.1 mmol) was dissolved in aqueous molar KOH (50 cm^3, pH 13.2) and O_3–O_2 was bubbled through for 30 min until the bright orange ruthenate solution was observed. The species was identified from its distinctive electronic spectrum (λ_{max}/nm: 462, 384) corresponding to that previously reported.[5,11]

$[Os^{VIII}O_4]$. *trans*-$[OsO_2(OH)_4]^{2-}$ (0.037 g, 0.1 mmol) was dissolved in neutral water (50 cm^3, pH 7) and O_3–O_2 bubbled through for 30 min until a very pale yellow coloured solution was observed. The species was identified from its electronic spectrum (λ_{max}/nm: 281, 250) corresponding to that previously reported.[13]

***cis*-$[Os^{VIII}O_4(OH)_2]^{2-}$.** *trans*-$[OsO_2(OH)_4]^{2-}$ (0.037 g, 0.1 mmol) was dissolved in aqueous molar KOH (50 cm^3, pH 13) and O_3–O_2 bubbled through for 30 min until a bright orange coloured solution was observed. The species was identified from its electronic spectrum (λ_{max}/nm: 380, 325, 255) corresponding to that previously reported.[1,12]

$[V^{V}O_4]^{3-}$. $VOSO_4$ (0.04 g, 0.25 mmol) was dissolved in aqueous molar KOH (50 cm^3, pH 13) and O_3–O_2 was bubbled through for 30 min until a colourless solution was observed. The species was identified from its electronic spectrum (λ_{max}/nm: 260) corresponding to that previously reported.[13]

Yields of the above species detected specrophotometrically are essentially quantitative.

[PPh$_4$]$_2$[Ru$_2$O(μ-OCOEt)$_2$Cl$_6$] 1. RuCl$_3$·3H$_2$O (0.026 g, 0.1 mmol) and excess PPh$_4$Cl (0.26 g, 0.6 mmol) were dissolved in propionic acid (25 cm^3) and O$_3$–O$_2$ was bubbled through the solution. After 30 min of ozonolysis the colour had changed to dark red. After cooling overnight at 4 °C orange-red crystals deposited and the crystal structure was determined (see Fig. 1). Yield 0.042 g, 0.34 mmol (68%). IR (in a liquid paraffin mull from 4000 to 300 cm^{-1}): 2726w, 2670w, 1643m, 1309m, 1151s, 1106m, 1056m, 1027s, 966w, 883s, 809m, 798m, 786m, 375s.

Crystal data for 1. [C$_6$H$_{10}$O$_5$Cl$_6$Ru$_2$][C$_{24}$H$_{20}$P]$_2$, $M = 1255.7$, monoclinic, $P2_1/n$ (no. 14), $a = 21.515(2)$, $b = 12.682(2)$, $c = 40.128(4)$ Å, $\beta = 90.06(1)°$, $U = 10973(2)$ Å^3, $Z = 8$ (there are two crystallographically independent molecules in the asymmetric unit), $D_c = 1.520$ g cm^{-3}, μ(Cu-Kα) = 80.6 cm^{-1}, $F(000) = 5072$, $T = 293$ K; orange-red platy needles, 0.43 × 0.07 × 0.03 mm, Siemens P4/RA diffractometer, ψ-scans, 15146 independent reflections. The data were corrected for Lorentz and polarisation factors, and a semi-empirical absorption correction (lamina, based on ψ-scans) was applied; the maximum and minimum transmission factors were 0.98 and 0.60. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised, assigned isotropic thermal parameters, [U(H) = 1.2U_{eq}(C), U(H) = 1.5U_{eq}(C–Me)], and allowed to ride on their parent atoms. Refinements were by full matrix least-squares based on F^2 to give $R1 = 0.068$, $wR2 = 0.145$ for 9373 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$] and 1052 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.61 and 0.71 e Å^{-3} respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.001 and 0.008 respectively. All computations were carried out using the SHELXTL PC program system.[35]

CCDC reference number 186/1152.

(b) Preparation of polyoxometalates

K$_6$[Mn^{IV}Mo$_9$O$_{32}$]·10H$_2$O. To an acetic acid–KOH buffer (pH 4.5, 50 cm^3) was added Na$_2$[MoO$_4$] (2.89 g, 12 mmol) and MnSO$_4$·4H$_2$O (0.223 g, 1 mmol) and O$_3$–O$_2$ was bubbled through the solution for 45 min after which time the solution had turned a dark red colour. On cooling to 4 °C overnight, red crystals of K$_6$[MnMo$_9$O$_{32}$]·10H$_2$O were deposited. Yield 1.3 g, 0.7 mmol (70%) based on the manganese starting material (Found: K, 15.1, Mn, 3.0, Mo, 47.4. Calc. for K$_6$H$_{20}$O$_{42}$-MnMo$_9$: K, 12.7, Mn, 3.0; Mo, 46.8%).

K$_8$[Mn^{IV}W$_6$O$_{24}$]·6H$_2$O. The same procedure was used as above but Na$_2$[WO$_4$] (3.9 g, 12 mmol) was used in place of Na$_2$[MoO$_4$]; the product was isolated as deep red crystals. The structure was confirmed by determination of the dimensions of the unit cell which were identical to those of the known compound.[21] Yield 0.63 g, 0.32 mmol (32%) based on the manganese starting material.

[NH$_4$]$_2$[Mn^{IV}Mo$_6$H$_6$O$_{24}$]·20H$_2$O. The salt [NH$_4$]$_4$[Mn^{II}Mo$_6$-H$_6$O$_{24}$]·5H$_2$O (0.1 g, 0.08 mmol) was prepared by the literature method[22] and dissolved in H$_2$O (50 cm^3). The O$_3$–O$_2$ mixture was then bubbled through this solution and the yellow colour gradually turned to bright red over a period of 30 min. The solution was filtered and the filtrate cooled at 4 °C after which time a red precipitate had deposited. Yield 0.06 g, 0.04 mmol (40%) based on the manganese starting material (Found: Mn, 3.5; Mo, 41.6. Calc. for N$_2$H$_{54}$O$_{44}$MnMo$_6$: Mn, 3.9; Mo, 40.6%).

Na$_8$[Ce^{IV}W$_{10}$O$_{36}$]·8H$_2$O. Na$_9$[Ce^{III}W$_{10}$O$_{36}$]·6H$_2$O (0.1 g, 0.03 mmol) was prepared by the literature method[15] and dissolved in water (50 cm^3); the pH was adjusted to 2 with concentrated HCl. The O$_3$–O$_2$ mixture was then bubbled through this solution and the pale beige colour gradually turned to bright yellow over a period of 30 min. Yield 0.1 g, 0.03 mmol (100%) (Found: Na, 6.3; Ce, 2.8; W, 64.0. Calc. for Na$_8$CeW$_{10}$O$_{44}$H$_{16}$: Na, 6.4; Ce, 4.9; W, 63.8%).

(c) Preparation of chloro complexes

[^{n}Bu$_4$N]$_2$[Pt^{IV}Cl$_6$]. To aqueous HCl (50 cm^3, pH 2) was added K$_2$[PtCl$_4$] (0.5 g, 1.2 mmol) and the solution was ozonised for 15 min until the initial orange colour had changed to pale yellow. Upon addition of (^{n}Bu$_4$N)Cl a yellow precipitate was deposited, filtered, washed with water and air dried. Yield 0.95 g, 1 mmol (89%) (Found: C, 42.6; H, 7.6; N, 3.1. Calc. for C$_{32}$H$_{72}$N$_2$PtCl$_6$: C, 43.2; H, 8.2; N, 3.2%).

[^{n}Bu$_4$N]$_2$[Pd^{IV}Cl$_6$]. To aqueous HCl (50 cm^3, pH 2) was added PdCl$_2$ (0.5 g, 2.8 mmol) and the solution was ozonised for 15 min until the initial red colour had changed to bright red. Upon addition of (^{n}Bu$_4$N)Cl a yellow precipitate was deposited, filtered, washed with water and air dried. Yield 1.85 g, 2 mmol (82%) (Found: C, 47.5; H, 9.0; N, 3.2. Calc. for C$_{32}$H$_{72}$N$_2$PdCl$_6$: C, 48.0; H, 9.1; N, 3.5%).

[^{n}Bu$_4$N]$_2$[Ir^{IV}Cl$_6$]·H$_2$O. To aqueous HCl (50 cm^3, pH 2) was added IrCl$_3$ (0.5 g, 1.7 mmol) and the solution was ozonised for 15 min until the initial dark green colour had changed to brown. Upon addition of (^{n}Bu$_4$N)Cl a yellow precipitate was deposited, filtered, washed with water and air dried. Yield 0.71 g, 0.8 mmol (46%) (Found: C, 41.9; H, 7.0; N, 3.7. Calc. for C$_{32}$H$_{74}$N$_2$IrCl$_6$O: C, 42.4; H, 8.2; N, 3.1%).

[Me$_4$N][Au^{III}Cl$_4$]. The complex [Me$_4$N][Au^{I}Cl$_2$], made by the method of Buckley *et al.*[28] (0.25 g, 0.6 mmol), was suspended in aqueous HCl (50 cm^3, pH 2) and ozonised for 30 min. The dark brown suspension gradually turned bright yellow. The solid was filtered and washed with cold water. Yield 0.24 g, 0.6 mmol (100%) (Found: C, 11.9; H, 2.9; N, 3.4. Calc. for C$_4$H$_{12}$NAuCl$_4$: C, 11.7; H, 2.9; N, 3.4%).

(d) Other preparations

[Mn^{III}(OAc)$_3$]·2H$_2$O. Mn^{II}(OAc)$_2$·4H$_2$O (2.45 g, 10 mmol) was suspended in glacial acetic acid (50 cm^3) and ozonised for 15 min. Immediately the suspension began to darken to a brown colour. After ozonation water (20 cm^3) was added and the solution left at 4 °C overnight whereupon a dark brown solid had deposited. Yield 1.9 g, 7 mmol (70%) (Found: C, 26.6; H, 4.8. Calc. for C$_6$H$_{13}$O$_8$Mn: C, 26.9; H, 4.9%).

***cis*-[Ru^{II}(bipy)$_2$(NCC$_6$H$_5$)$_2$][PF$_6$]$_2$·3H$_2$O.** *cis*-[Ru^{II}(bipy)$_2$-(NH$_2$CH$_2$C$_6$H$_5$)$_2$][PF$_6$]$_2$ (0.5 g, 0.8 mmol), made by the literature procedure,[1,32] was dissolved in CH$_2$Cl$_2$ (50 cm^3) and O$_3$–O$_2$ bubbled through this solution. After 10 min the initial dark red colour turned yellow and on standing a gold precipitate deposited. This was filtered off, washed with water and dried in air. Raman spectroscopy and elemental analyses showed the presence of the desired product. Yield 0.45 g, 0.45 mmol (56%) (Found: C, 42.1; H, 3.0; N, 8.6. Calc. for C$_{34}$H$_{32}$N$_6$RuP$_2$F$_{12}$O$_3$: C, 42.3; H, 3.4; N, 8.7%).

Acknowledgements

We thank Air Products and Chemicals Inc. for a postdoctoral grant to A. J. B., and Johnson Matthey Ltd. for loans of osmium tetraoxide and ruthenium trichloride. We are grateful to Dr. Fran J. Waller (APCI) for helpful discussions and the

University of London Intercollegiate Research Service (ULIRS) for the Raman instrument.

References

1 Part 18, W. P. Griffith, B. Reddy, A. G. F. Shoair, M. Suriaatmaja, A. J. P. White and D. J. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2819.
2 A. J. Bailey, M. G. Bhowon, W. P. Griffith, A. G. F. Shoair, A. J. P. White and D. J. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3245.
3 A. J. Bailey, L. D. Cother, W. P. Griffith and D. M. Hankin, *Transition Met. Chem.*, 1995, **20**, 590; W. P. Griffith, *Chem. Soc. Rev.*, 1992, **21**, 179.
4 S. V. Ley, J. Norman, W. P. Griffith and S. P. Marsden, *Synthesis*, 1994, 639.
5 A. J. Bailey, W. P. Griffith, S. I. Mostafa and P. A. Sherwood, *Inorg. Chem.*, 1993, **32**, 268.
6 G. W. Bushnell and M. A. Khan, *Can. J. Chem.*, 1972, **50**, 315.
7 L. Chugaev and W. Chlopin, *Z. Anorg. Allg. Chem.*, 1926, **15**, 253.
8 D. B. Currie, A. L. Hector, W. Levason and M. Thomas, *J. Mater. Chem.*, 1997, **7**, 1871.
9 M. Wu, J. Long, X. Li, A. Huan and Y. Luo, *Zhongshan Daxue Xuebao*, *Ziran Kexueban*, 1997, **36**, 129 (*Chem. Abstr.*, 1997, **127**, 242428d).
10 Y. M. Kiselev, D. A. Pankratov, L. A. Shundrin and I. N. Kiseleva, *Russ. J. Inorg. Chem.*, 1996, **41**, 1963; Y. M. Kiselev, D. A. Pankratov, N. A. Ezerskaya, I. N. Kiseleva, L. A. Shundrin and M. P. Popovich, *ibid.*, 1994, **39**, 1278.
11 R. E. Connick and C. R. Hurley, *J. Am. Chem. Soc.*, 1952, **74**, 5012.
12 J. S. Mayell, *Ind. Eng. Chem. Prod. Res. Dev.*, 1968, **7**, 129.
13 R. H. Petit, B. Brist, A. Mullerand and E. Diemann, *Mol. Phys.*, 1974, **27**, 1373.
14 W. P. Griffith and J. M. Jolliffe, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 3483; W. P. Griffith, J. M. Jolliffe, S. V. Ley and D. J. Williams, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1219.
15 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2285.
16 P. Neubold, K. Wieghardt, B. Nuber and J. Weiss, *Angew Chem.*, *Int. Ed. Engl.*, 1988, **27**, 933.
17 C. Sudha and A. R. Chakravorty, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3289.
18 R. Neumann, *Prog. Inorg. Chem.*, 1998, **47**, 317; I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171; D. E. Katsoulis, *ibid.*, 359.
19 R. Neumann and D. Jowiler, *Tetrahedron*, 1996, **52**, 8781.
20 S. J. Dunne, R. C. Burns, T. W. Hambley and G. A. Lawrence, *Aust. J. Chem.*, 1992, **45**, 685.
21 V. S. Sergienko, U. N. Molchanon, M. A. Porai-Koshits and E. A. Torchenkova, *Sov. J. Coord. Chem.*, (*Engl. Transl.*), 1979, **5**, 940.
22 A. Ginestra, F. Giannetta and F. Fiorucci, *Gazz. Chim. Ital.*, 1968, **98**, 1197.
23 R. D. Peacock and T. J. R. Weakley, *J. Chem. Soc. A*, 1971, 1836.
24 K. Ito, D. Nakamura, Y. Kuriuta, K. Ito and M. Kubo, *J. Am. Chem. Soc.*, 1961, **83**, 4526.
25 A. D. Westland and N. C. Bhiwandker, *Can. J. Chem.*, 1961, **39**, 2353.
26 E. E. Kim, K. Eriks and R. Magnuson, *Inorg. Chem.*, 1984, **23**, 393.
27 K.-F. Tebbe and H. G. van Schnering, *Z. Anorg. Allg. Chem.*, 1973, **396**, 66.
28 R. W. Buckley, P. C. Healy and W. A. Loughlin, *Aust. J. Chem.*, 1997, **50**, 775.
29 P. J. Andrulis, M. J. S. Dewar, R. Dietz and R. L. Hunt, *J. Am. Chem. Soc.*, 1966, **88**, 5473.
30 M. Sem, *Z. Elektrochem.*, 1915, **21**, 426.
31 I. W. Hessel and C. Romers, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 545.
32 F. R. Keene, D. J. Salomon and T. J. Meyer, *J. Am. Chem. Soc.*, 1976, **98**, 1884.
33 G. Milazzo and S. Caroli, *Tables of Standard Electrode Potentials*, Wiley, London, 1978, pp. 229, 239.
34 A. Vogel, *Textbook of Quantitative Inorganic Analysis*, Longman, London, 4th edn., 1978, p. 379.
35 SHELXTL PC version 5.03, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994.

Paper 8/06086J