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HIGH-VALENT COMPLEXES OF RUTHENIUM AND OSMIUM

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I. Introduction

The study of high-valent complexes of osmium and ruthenium, especially those involving multiple bonding to heteroatoms, has greatly expanded during the past decade. Osmium and ruthenium, being distinguished from other elements by the variety of the oxidation states they display in their complexes, have attracted a plethora of study on their coordination chemistry. In this review, we will focus on the high oxidation state chemistry of osmium and ruthenium, that is, those complexes with oxidation states of +IV to +VIII.

The high-valent chemistry of osmium and ruthenium has been largely dominated by complexes containing multiply bonded ligands, such as oxo, nitrido, and imido ligands. Among the types of multiply bonded ligands, oxo compounds have been known the longest and their chemistry has been most extensively developed. The proliferating study of transition metal complexes containing these multiply bonded ligands has been attributed to the growing recognition of their role in heterogeneous, homogeneous, and enzymatic catalysis. Examples include oxidation, ammoxidation, and nitrogen fixation reactions. Interest in these materials also stems from their possible applications as photocatalysts and as electronic materials, in particular the oxo and nitrido moieties.

In this review, the materials have been organized according to the formal oxidation states of the metal and the discussions will focus mainly on the structural as well as reactivity patterns of these complexes. In order to keep the material within bounds we consider only those complexes that may reasonably be considered to involve discrete molecular units, having metal–ligand multiple bonding. Polynuclear derivatives in which the ligand bridges two or more metals will also be mentioned. We have attempted to make our coverage of the recent literature on high-valent chemistry of ruthenium coordination complexes with various classes of ligands as comprehensive as possible. The chemistry of high-valent osmium complexes will also be mentioned but to a lesser extent than that of ruthenium. Organometallic complexes will only be selectively covered. The literature citation is not exhaustive, but aims to include important studies on the most recent work. The recent applications of high-valent osmium and ruthenium complexes to organic oxidation can be found in two review articles by Griffith and co-workers (*1*).

II. Ruthenium and Osmium Complexes Containing Multiple Bonds to Heteroatoms

Metal–ligand multiple bonds consist of a σ component with one or two additional π bonds involving the overlap between ligand p and metal d orbitals. It is the presence of this $d\pi$–$p\pi$ overlap that provides the stabilizing ability for metals in high oxidation states. With the ligand p orbitals being more low-lying in energy than the metal d orbitals, effective $d\pi$–$p\pi$ overlap requires that the metal d orbitals be empty or partially filled. Thus complexes with significant metal–ligand multiple bonds are commonly found for metal centers with an oxidation state of no less than +IV and no more than four d electrons (*2, 3*).

The oxo group is formally a four- or six-electron donor. Nitrido, imido, and alkylidyne ligands can also function as four- or six-electron donors and are isoelectronic with the oxo moiety, with one filled orbital of σ symmetry and two filled p orbitals of π symmetry lying perpendicular to the metal–ligand bond axis. The alkylidene group differs from the above ligands in that it can form at most a double bond and is similar to the others in the sense that it is a four-electron donor. There is, however, no clear-cut example on high-valent ruthenium and osmium alkylidene complexes. Complexes containing the Ru=CRR′ unit are known but they are often referred to as carbene species (*4*).

Comparisons between the various isoelectronic π-donor ligands have previously been made by Griffith (*5*) and the structures of transition-metal complexes containing multiply bonded ligands have been compiled by Nugent and Mayer (*2*). In general, the nitrido ligand is the strongest π-bonding ligand of all. This has been supported both by relative bond distance arguments and by spectroscopic studies. The relative bond strengths (based on relative bond distance arguments) have been suggested by Nugent and Haymore (*3*) to follow the order $M{\equiv}N > M{\equiv}O > M{\equiv}NR$. Comparative studies on the reactivity and electrochemical oxidation potentials of isoelectronic nitrido, methyimido, and oxo complexes of osmium(VI) by Marshman and Shapley (*6*) showed that the osmium–ligand bond strength decreases in the order Os—N > Os—NMe > Os—O, and a difference in relative reactivities of the oxo, nitrido, and methylimido complexes toward electrophiles and nucleophiles has been observed. As a general rule, oxo groups, being most electronegative, form the most polar bonds, whereas metal–carbon bonds are the most covalent, consistent with the much lower electronegativity of carbon. The ambiguity in assigning oxidation states that is often encountered with alkylidyne and alkylidene compounds is also a result of the lower electronegativity of carbon. The alkylidyne ligands can only be considered as CR^{3-} in high oxidation state complexes of electropositive metals. Similarly, alkylidene ligands are best described as CR_2^{2-} only when they lack heteroatom substituents and are bound to high oxidation state metal centers (Schrock-type alkylidene ligands). Ruthenium and osmium complexes containing a $M{\equiv}CR$ moiety are often referred as carbyne complexes; their chemistry and structures can be found in a review article by Gallop and Roper (*4*) and will not be considered here.

In general, as we go through the various oxidation states in this review, we will come to see that corresponding oxidation states are less stable in ruthenium than in osmium. This has partially been attributed to the lower ioinization potentials for the corresponding oxidation states of a 5*d* element compared to a 4*d* element.

A. OXIDATION STATE +IV

1. *Oxo Complexes*

a. Oxides, Oxoanions, and Oxohalides. Ruthenium(IV) oxide, RuO_2, has been prepared by the high-temperature oxidation of ruthenium metal in oxygen (*7, 8*) or ruthenium(III) chloride (*9*). The X-ray crystal structure has been obtained: tetragonal with a rutile structure, *d*(Ru—O) = 1.984(6) and 1.942(10) Å (*10*). No significant metal–metal bonding is observed (closest Ru···Ru distance, 3.107 Å) (*11*). Similar rutile structures have also been observed for both forms of osmium(IV) oxide, OsO_2: the brown form obtained from Os and OsO_4 at ~600°C and the black form by heating $K_2[OsCl_6]$ and KOH at 500°C (*12*). Structural data for the brown OsO_2 were obtained: *d*(Os—O) = 2.006(8) and 1.962(13) Å; closest Os···Os distance, 3.184 Å (*13*).

Compounds of the type $M_2{}^{I}RuO_3$ and $M^{II}RuO_3$ (M^{I} = Li, Na, K; M^{II} = Ca, Sr, Ba) have been prepared and studied (*14*). Osmates(IV) of $M_2{}^{I}OsO_3$ and $M^{II}OsO_3$ are also known (M^{I} = Li, Na; M^{II} = Ca, Sr, Ba) (*15*). The $M^{II}[MO_3]$ compounds (M^{II} = Ca, Sr; M = Ru, Os) have perovskite structures (*16*), whereas $Ba[MO_3]$ has a hexagonally distorted perovskite structure (*17*). The physical and magnetic properties of mixed oxides such as $Na[Ru_2O_4]$, the ruthenium bronzes $Na_{3-x}[Ru_4O_9]$, $Sr_2[RuO_4]$, and $M_2{}^{III}[Ru_2O_7]$ have been reviewed elsewhere (*14*). Recently, the single-crystal structure investigation of a new mixed-valence complex $Ba_7Ru_4O_{15}O_2Cl_2$ having relatively short Ru—Ru separation (2.725 Å) was reported (*18*). In this compound, two kinds of ruthenium ions, Ru(IV) and Ru(V), are located in the octahedral holes of the oxygen framework, with Ru(IV)—O and Ru(V)—O distances being 1.966(8)–1.9779(8) Å and 1.877(8)–2.096(8) Å, respectively.

There have been claims for Ru_2OCl_6 (*14*), $RuOCl_2$ (*14*), Ru_2OCl_5 (*14*), and Os_2OCl_6 (*19*). The single-crystal X-ray structure of $K_4[Ru_2OCl_{10}]$ shows the anion to have a μ-oxo-bridged structure with the equatorial chloro ligands in the eclipsed position. The Ru—O distance is 1.801(2) Å with a Ru—O—Ru angle of 180° (*20*). The structure of $Cs_4[Os_2OCl_{10}]$ is similar: *d*(Os—O) = 1.778(15) Å with the Os—O—Os angle at 180° (*21*). A few other μ-oxo halo complexes have also been reported. Examples include $[Ru_2OBr_{10}]^{4-}$ (*15*), $[Ru_2OF_{10}]^{4-}$ (*15*), and $[Os_2OI_{10}]^{4-}$ (*22*).

b. Group IV Ligands. No ruthenium(IV) nor osmium(IV) oxo complexes with this group of ligands have yet been reported.

c. Group V Ligands. Extensive works on $Ru^{IV}{=}O$ complexes containing nonlabile oxidation-resistant nitrogen donor ligands have been reported (*1, 23, 24*). In general, these complexes are prepared by either oxidation of $Ru^{II}—OH_2$ and $Ru^{III}—OH_2$ precursors (*25–30*) or reduction of *trans*-dioxoruthenium(VI) (*31–33*). Selected examples are depicted as follows:

$$[Ru^{II}(trpy)(diamine)(H_2O)]^{2+} + 2Ce^{IV} \xrightarrow{H_2O} [Ru^{IV}(trpy)(diamine)(O)]^{2+} + 2Ce^{III} + 2H^{+}$$

$$[Ru^{III}(14TMC)(OH)(OH_2)]^{2+} + X \xrightarrow{[O]} [Ru^{IV}(14TMC)(O)(X)]^{n+}$$

$$(X = NCO^-, N_3^-, n = 1; X = H_2O, n = 2)$$

$$[Ru^{VI}(14TMC)(O)_2]^{2+} + PPh_3 \xrightarrow{CH_3CN} [Ru^{IV}(14TMC)(O)(CH_3CN)]^2 + O{=}PPh_3$$

$$[Ru^{VI}(TMP)(O)_2] + PPh_3 \xrightarrow{CH_2Cl_2} [Ru^{VI}(TMP)(O)] + O{=}PPh_3$$

Six-coordinated $Ru^{IV}{=}O$ complexes are paramagnetic with measured μ_{eff} ranging from 2.7 to 2.95 μ_B at room temperature. Their IR spectra exhibit a Ru=O stretch ranging from 750 to 845 cm^{-1} (Table I). The first complex of this type is $[Ru(bpy)_2(py)(O)](ClO_4)_2$, prepared by either Ce(IV) or electrochemical oxidation of $[Ru(bpy)_2(py)(OH_2)](ClO_4)_2$ (*25, 26*). The ^{18}O-labeling study has been performed to allow the assignment of the $\nu(Ru{=}O)$ stretch (*26*). Its room temperature magnetic moment is 2.94 μ_B. Detailed studies on the temperature variation of the magnetic susceptiblity revealed a $[(d_{xy})^2(d_{xz})^1(d_{yz})^1]$ triplet ground state with the first excited state lying 79 cm^{-1} higher in energy in the solid state and 56 cm^{-1} in solution (*34*). The $[Ru(bpy)_2(py)(O)]^{2+}$ complex was found to be unstable, owing to the slow loss of pyridine ligand to form a deep green, oxo-bridged dimeric species, suggested to be $[(bpy)_2(OH_2)RuORu(py)(bpy)_2]^{4+}$ (*26, 35*). To overcome this instability problem, the $[Ru(trpy)(R\text{-}bpy)(O)]^{2+}$ (*36*), $[Ru(tpm)R\text{-}bpy)(O)]^{2+}$ (*37*), and *cis*- and *trans*-$[Ru(trpy)(pic)(O)]^+$ (*37*) complexes

TABLE I

SELECTED METAL–OXO BOND DISTANCES AND STRETCHING FREQUENCIES FOR RUTHENIUM AND OSMIUM OXO COMPLEXES

Complex	$d(M{=}O)$, Å	$\nu_{as}(M{=}O)$, cm^{-1}	Ref.
$[Ru^{IV}(bpy)_2(py)(O)](ClO_4)_2$	—	792	*26*
$[Ru^{IV}(bpy)_2(py)(^{18}O)](ClO_4)_2$	—	752	*26*
$[Ru^{IV}(trpy)(bpy)(O)](ClO_4)_2$	—	792	*36*
$[Ru^{IV}(py)_4(O)Cl]ClO_4$	1.862(8)	800	*38*
$[Ru^{IV}(14TMC)(O)(MeCN)](PF_6)_2$	1.765(5)	815	*30, 31*
$[Ru^{IV}(14TMC)(O)Cl]ClO_4$	1.765(7)	815	*30, 31*
$[Ru^{IV}(14TMC)(O)(NCO)]ClO_4$	1.765(5)	815	*30*
$[Ru^{IV}(14TMC)(O)(N_3)]ClO_4$	1.765(5)	815	*30*
$[Ru^{IV}(15TMC)(O)Cl]ClO_4$	—	820	*30*
$[Ru^{IV}(16TMC)(O)Cl]ClO_4$	1.75(1)	840	*41*
$[Ru^{IV}(TMEA)_2(O)Cl]ClO_4$	—	820	*30*
$[Ru^{IV}(CRMe_3)(O)(NCO)]ClO_4$	1.777(2)	790	*32*

(*continued*)

TABLE I *Continued*

Complex	d(M=O), Å	ν_{as}(M=O), cm^{-1}	Ref.
$[Ru^{IV}(trpy)(TMEA)(O)](ClO_4)_2$	—	773	*28*
$[Ru^{IV}(trpy)(6,6'\text{-}Cl_2bpy)(O)](ClO_4)_2$	—	799	*29*
$[Ru^{IV}(N_2O_2)(O)(H_2O)](ClO_4)_2$	1.739(2)	845	*46*
$[Ru^{IV}(TMP)(O)]$	—	823	*33*
$[Ru^{IV}(TMP)(^{18}O)]$	—	782	*33*
$[Ru^{IV}(bpy)_2(PEt_3)(O)](ClO_4)_2$	—	790	*42*
$[Ru^{IV}(bpy)_2(PEt_3)(^{18}O)](ClO_4)_2$	—	750	*42*
$[Ru^{IV}(bpy)_2(P^iPr_3)(O)](ClO_4)_2$	—	790	*42*
$[Ru^{IV}(bpy)(biq)(P^nPr_3)(O)](ClO_4)_2$	—	785	*27*
$[Ru^{V}(O)(O_2COCEt_2)_2](^nPr_4N)$	1.687(6)	900	*147*
$[Ru^{V}(N_4O)(O)](ClO_4)_2$	—	872	*45*
$[Ru^{V}(CH_2SiMe_3)_3(O)]_2$	1.733(6)	908	*130*
$[L_{OEt}(O)Ru(\mu\text{-}O)_2Ru(O)L_{OEt}]$	1.725(3)	848	*149*
trans-$[Ru^{V}(14TMC)(O)_2]ClO_4$	—	840–860	*30*
cis-$[Ru^{V}(Tet\text{-}Me_6)(O)_2]ClO_4$	1.751(4) 1.754(4)	818	*134*
$[Ru^{VI}(O)(CH_2SiMe_3)_4]$	—	1045	*178*
$[Ru^{VI}(O)_3(OH)_2]Ba$	1.751 1.759	820	*153*
$[Ru^{VI}(O)_2Cl_3][N(PPh_3)_2]$	1.658(5) 1.694(7)	878 (ν_{sym} 891)	*168*
$[Ru^{VI}(O)_2Cl_4][N(PPh_3)_2]_2$	1.709(4)	830	*168*
$NaK_5[Ru^{VI}HIO_6)_2(O)_2]\cdot 8H_2O$	1.732(8)	820	*235*
$K_6[Ru^{VI}(H_2TeO_6)_2(O)_2]\cdot 4H_2O$	—	825	*235*
trans-$[Ru^{VI}(14TMC)(O)_2](ClO_4)_2$	—	855	*204*
trans-$[Ru^{VI}(15TMC)(O)_2](ClO_4)_2$	1.718(5)	855	*204*
trans-$[Ru^{VI}(16TMC)(O)_2](ClO_4)_2$	1.705(7)	860	*204*
trans-$[Ru^{VI}(CRMe_3)(O)_2](ClO_4)_2$	—	860	*32*
trans-$[Ru^{VI}(pytn)(O)_2](ClO_4)_2$	—	860	*203*
trans-$[Ru^{VI}(N_2O_2)(O)_2](ClO_4)_2$	—	865	*46*
trans-$[Ru^{VI}(py)_2(OAc)_2(O)_2]$	1.726(1)	840	*190*
trans-$[Ru^{VI}(bpy)_2(O)_2](ClO_4)_2$	—	850	*193*
trans-$[Ru^{VI}(trpy)(O)_2(H_2O)](ClO_4)_2$	1.661	834, 841	*188*
trans-$[Ru^{VI}(TMP)(O)_2]$	—	821	*218*
trans-$[Ru^{VI}(TPP)(O)_2]$	—	819	*67*
trans-$[Ru^{VI}(OEP)(O)_2]$	—	821	*67*
cis-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2(O)_2](ClO_4)_2$	—	790 (ν_{sym} 840)	*195*
cis-$[Ru^{VI}(2,9\text{-}Me_2phen)_2(O)_2](PF_6)_2$	—	787 (ν_{sym} 839)	*196*
cis-$[Ru^{VI}(Tet\text{-}Me_6)(O)_2](ClO_4)_2$	1.795(9)	855 (ν_{sym} 874)	*134*
$[Ru^{VI}(O)_2Cl_2(4\text{-}^tBu\text{-}py)_2]\cdot H_2O$	—	842 (ν_{sym} 858)	*187*
$[Ru_2{}^{VI}O_6(py)_4]\cdot 3\cdot 5H_2O$	1.72(1)	810 (ν_{sym} 826)	*183*

TABLE I *Continued*

Complex	d(M=O), Å	ν_{as}(M=O), cm^{-1}	Ref.
trans-$[Os^{V}(14TMC)(O)_2]ClO_4$	—	873, 879	*75*
$[Os^{VI}(O)\{NHC(Me)_2C(Me)_2NH\}$-$\{NH_2C(Me)_2C(Me)_2NH\}]ClO_4$	1.72(2)	920	*210*
$[OS^{VI}(O)(O_2C_6H_{10})(NC_7H_{13})]_2(\mu\text{-}O)_2$	1.73	879 (ν_{sym} 923)	*131*
cis-$[Os^{VI}(O)_2(OAc)_3]K\cdot 2AcOH$	1.711	845	*240*
$[Os^{VI}(O)_2(O_2C_2H_4)_2]K_2$	—	803 (ν_{sym} 859)	*182*
trans-$[Os^{VI}(O)_2$(R-cat)$(py)_2]$	—	820 (ν_{sym} 860)	*255*
cis-$[Os^{VI}(O)_2(S_2O_3)_2]Na_2$	1.692(3)	915 (ν_{sym} 931)	*256*
trans-$[Os^{VI}(O)_2(OH)_2(phen)]$	1.737(4) 1.747(4)	850 (ν_{sym} 895)	*201*
trans-$[Os^{VI}(O)_2(en)_2](HSO_4)_2$	1.74(1)	(ν_{sym} 917)	*208*
trans-$[Os^{VI}(O)_2(CN)_4]Cs_2$	1.750(8)	840	*171*
trans-$[Os^{VI}(O)_2(bpy)_2]^{2+}$	—	872	*74*
cis-$[Os^{VI}(O)_2(bpy)_2]^{2+}$	—	863 (ν_{sym} 883)	*74*
trans-$[Os^{VI}(O)_2(14TMC)](ClO_4)_2$	—	875	*75, 211*
trans-$[Os^{VI}(O)_2(15TMC)](ClO_4)_2$	—	875	*75*
trans-$[Os^{VI}(O)_2(16TMC)](ClO_4)_2$	—	875	*75*
cis-$[Os^{VI}(O)_2(mes)_2]$	1.690(7) 1.700(7)	918 (ν_{sym} 950)	*176*
$[Os^{VI}(O)(CH_2SiMe_3)_4]$	1.692(6)	1040 1054	*177*
$[Os^{VI}(O)_2(mes)_2(2,6\text{-}Me_2C_6H_3NC)]$	—	911 (ν_{sym} 957)	*179*
trans-$[Os^{VI}(O)_2(mes)_2(bpy)]$	—	857	*179*
cis-$[Os^{VI}(O)_2(mes)_2(PMePh_2)_2]$	—	940 (ν_{sym} 955)	*179*
$[Os^{VI}(O)(NBu^t)(mes)_2]$	1.739(12)	955	*179*
$[Os^{VI}(O)Me_4]$	1.681(4)[a]	1013	*180*
$[Os^{VI}(O)_2(Me)_2(py)_2]$	1.723(3) 1.715(3)	866	*181*
trans-$[Os^{VI}(p\text{-}MeTPP)(O)_2]$	1.743(3)	843	*221*
trans-$[Os^{VI}(3\text{-}t\text{-}Bu\text{-}saltmen)(O)_2]$	1.760(7) 1.722(8)	845	*229*
trans-$[Os^{VI}(\eta^4CHBA\text{-}Et)(O)_2]K_2$	—	820	*230*
trans-$[Os^{VI}(\eta^4CHBA\text{-}Et)(^{18}O)_2]K_2$	—	782	*230*
trans-$[Os^{VI}(PPh_3)_2(O)_2Cl_2]$	—	840	*232*
$[Os_2^{VI}O_6(py)_4]$	1.73	833 (ν_{sym} 875)	*184*
$[Os_2^{VI}O_6(NO_2)_4]K_4\cdot 6H_2O$	1.79(1)	841 (ν_{sym} 884)	*186, 302*

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[a] Determined from electron diffraction.

(R-bpy = substituted bipyridine; tpm = tris(1-pyrazolyl)methane; pic = picolinate anion), where substitutional instability is avoided by the chelate effect, were synthesized in a manner similar to that of $[Ru(bpy)_2(py)(O)]^{2+}$. The isolation of $[Ru(py)_4(O)Cl]ClO_4$ through NaOCl oxidation of *trans*-$[Ru^{II}(py)_4(NO)Cl](ClO_4)_2$ and disproportionation of $[Ru^{III}(py)_4(NO_2)Cl]^+$ has been reported by Mukaida and co-workers (*38–40*). Interestingly, *trans*-$[Ru^{IV}(py)_4(O)Cl]ClO_4$ has a very long Ru═O distance [d(Ru═O) = 1.862(8) Å] (*38*), and yet it has a ν(Ru═O) stretching frequency ν(Ru═O) = 800 cm^{-1}] similar to that found for *trans*-$[Ru^{IV}(L)(O)(X)]^{n+}$ (815–820 cm^{-1}) (*30*) and *trans*-$[Ru^{IV}(trpy)(bpy)(O)](ClO_4)_2$ (792 cm^{-1}) (*36*). Disproportionation of Ru(III)—NO_2 to Ru(IV)═O and Ru(II)—NO complexes containing macrocyclic tertiary amine ligand has also been observed. Treatment of *trans*-$[Ru(16TMC)Cl_2]^+$ with $NaNO_2$ in water gave $[Ru^{IV}(16TMC)(O)Cl]^+$, of which a Ru═O distance of 1.75(1) Å has been reported (*41*). Takeuchi prepared ruthenium(IV) oxo complexes containing 2,2′-bipyridine and 2,2′-biquinoline ligands (*27*) with mixed pnictogen ligand, $[Ru(bpy)_2(PnR_3)(O)]^{2+}$ and $[Ru^{IV}(bpy)(biq)(PnR_3)(O)]^{2+}$ (PnR_3 = tertiary phosphine or arsine) (*42, 43*). Although tertiary phosphine ligands are extremely susceptible to oxidation, these ligands have proven to be very stable within the coordination sphere of the Ru(IV) center. These complexes are powerful oxidants that oxidize a wide variety of organic substrates. Ru^{IV}═O complexes containing chelating ditertiary amines such as $[Ru^{IV}(trpy)(TMEA)(O)]^{2+}$ (*28*) and $[Ru^{IV}(trpy)(tmcn)(O)]^{2+}$ (TMEA = N,N,N',N'-tetramethylethylenediamine; tmcn = N,N,N',N'-tetramethyl-cyclohexanediamine) (*44*) have been prepared by cerium(IV) oxidation of the parent Ru^{II}—OH_2 precursors.

A ruthenium(IV) oxo complex containing pyridyl-type ligands, $[Ru^{IV}(N_4O)(O)]^+$, has been generated by electrochemical oxidation of $[Ru^{III}(N_4O)(OH_2)]^{2+}$ in aqueous solution (pH > 3.5). No isolation has been reported and this Ru(IV) oxo species was found to disproportionate to Ru(III) and Ru(V) in acidic solution (*45*).

A ruthenium(IV) oxo complex, $[Ru^{IV}(trpy)(6,6'\text{-}Cl_2bpy)(O)]^{2+}$ (6,6′-Cl_2bpy = 6,6′-dichloro2,2′-bipyridine), containing oxidative robust ligand has been found to be an active catalyst for the oxidation of saturated hydrocarbons by *tert*-butyl hydroperoxide (*29*). This Ru(IV) oxo complex has a very high E^0[Ru(IV)/(III)] of 1.13 V vs SCE at pH 1.0 and is capable of oxidizing the tertiary C—H bond of adamantane to give adamantan-1-ol exclusively.

An extensive series of Ru(IV) oxo complexes containing macrocyclic tertiary amine ligands, *trans*-$[Ru^{IV}(L)(O)(X)]^{n+}$ (L = 14TMC, 15TMC, 16TMC, $(TMEA)_2$; n = 1, X = Cl, N_3, NCO; n = 2, X = CH_3CN), has been prepared by Che and co-workers (*30*). The X-ray crystal structures of *trans*-$[Ru^{IV}(L)(O)(X)]^{n+}$ have been determined (Fig. 1). The Ru=O bond distance for all the complexes studied was found to be 1.765(5) Å, being relatively insensitive to the nature of X (*30–32*). A Ru(IV) oxo complex of pyridyl macrocycle, $[Ru^{IV}(CRMe_3)(O)(NCO)]ClO_4$, has been prepared by H_2O_2 oxidation of $[Ru^{III}(CRMe_3)(OH)(OH_2)]^{2+}$ in the presence of NaNCO. X-ray crystal structure revealed a Ru=O distance of 1.777(2) Å (*32*).

An oxoaquaruthenium(IV) complex of a macrocyclic mixed N,O-donor ligand, $[Ru^{IV}(N_2O_2)(O)(H_2O)]^{2+}$ (N_2O_2 = 1,12-dimethyl-3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane), has been prepared by electrochemical oxidation of $[Ru^{III}(N_2O_2)(OH)(OH_2)]^{2+}$ and characterized by X-ray crystallography (Fig. 2) (*46*). Isolation of this complex from aqueous solution has been taken as an indication of a very small equilibrium constant for the reaction

$$[O{=}Ru^{IV}{-}OH_2]^{2+} \rightleftharpoons [HO{-}Ru^{IV}{-}OH]^{2+}$$

This complex shows an exceptionally high Ru=O stretching frequency of 845 cm^{-1} (*46*). The stronger Ru=O bond is also consistent with the measured Ru=O distance of 1.739(2) Å (*46*), the shortest one ever reported for oxoruthenium(IV) complexes. The difference in the *d*(Ru=O) values in *trans*-$[Ru^{IV}(N_2O_2)(O)(H_2O)]^{2+}$ and $[Ru^{IV}(14TMC)(O)(X)]^{n+}$ has been discussed in terms of the weaker donor strength of

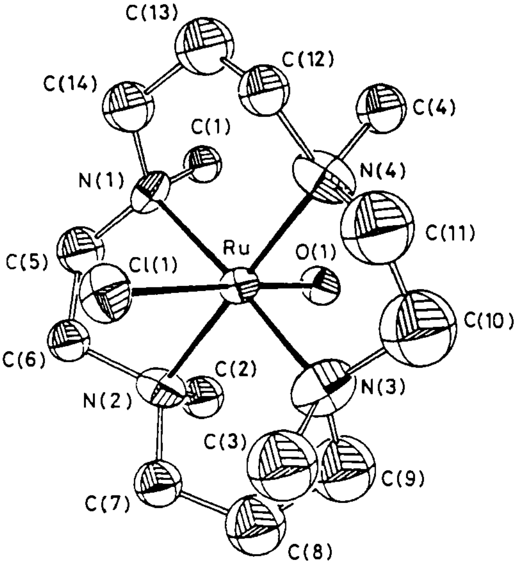


FIG. 1. A perspective view of the $[Ru^{IV}(14TMC)(O)Cl]^{+}$ cation with atom labeling. From Ref. (*204*).

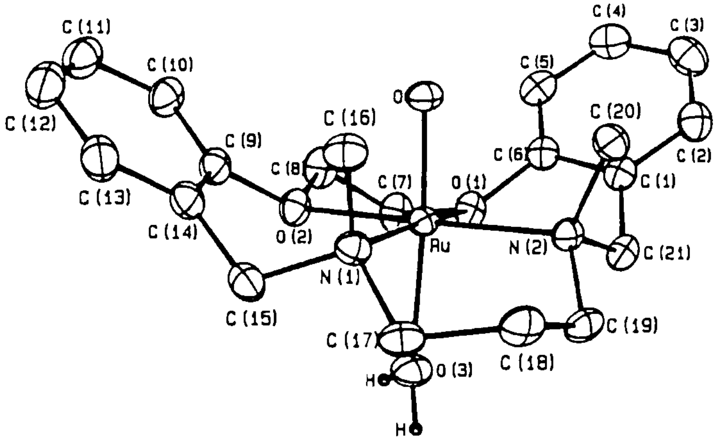


FIG. 2. ORTEP plot of the *trans*-$[Ru^{IV}(N_2O_2)(O)(OH_2)]^{2+}$ cation with atomic numbering scheme. From Ref. (*46*).

N_2O_2 than 14TMC, leading to an enhanced $p_\pi(O)—d_\pi(Ru)$ π-bonding interaction. A summary of the $d(Ru{=}O)$ and $\nu(Ru{=}O)$ data is collected in Table I.

The reactivities of oxoruthenium(IV) complexes have also been studied in detail. The oxidation of triphenylphosphine by $[Ru(bpy)_2(py)(O)]^{2+}$ has been studied in acetonitrile solution. An ^{18}O-labeling experiment shows that oxygen transfer from $Ru(IV){=}O$ to PPh_3 is quantitative (*47*). The observation of $[Ru^{II}(bpy)_2(py)(OPPh_3)]^{2+}$ as an intermediate suggests that the reaction proceeds via an initial redox step $[Ru^{IV}(bpy)_2(py)(O)]^{2+} + PPh_3 \rightarrow [Ru^{II}(bpy)_2(py)(OPPh_3)]^{2+}$, the reaction being first order in both reactants with $k = 1.75 \times 10^5\ M^{-1}\ s^{-1}$:

$$[Ru(bpy)_2(py)(O)]^{2+} + PPh_3 \xrightarrow{\text{fast}} [Ru(bpy)_2(py)(OPPh_3)]^{2+}$$

Similar reaction pathways have also been found for the oxidation of dimethyl sulfide to dimethyl sulfoxide and dimethyl sulfoxide to dimethyl sulfone by $[Ru(bpy)_2(py)(O)]^{2+}$ with respective rate constants of 17.1 and 0.13 $M^{-1}\ s^{-1}$ in MeCN at 298 K (*48*). The complex $[Ru(bpy)_2(py)(O)]^{2+}$ has also been used electrocatalytically for the oxidation of alcohols, aldehydes, alkenes, and aromatics (*23, 49*). The kinetics of oxidation of formic acid/formate ion by $[Ru(bpy)_2(py)(O)]^{2+}$, with a large kinetic isotope effect $[k_{HCO_2^-}/k_{DCO_2^-} = 19$ (25°C, $\mu = 1.0\ M$)], has been reported (*50*). A two-electron hydride transfer has been suggested for the oxidation of HCO_2^- by $[Ru(bpy)_2(py)(O)]^{2+}$. A similar mechanism has also been suggested for the oxidation of alcohols (*51*) and aromatics (*52*) by $[Ru(bpy)_2(py)(O)]^{2+}$ and other related Ru(IV) oxo complexes (*28,* *29, 43*). For the oxidation of benzyl alcohols, large C—H kinetic isotope effects ranging from 50 to 36 have been found (*29, 43*). Oxidation of methanol by $[Ru(bpy)_2(py)(O)]^{2+}$ also shows a C—H kinetic isotope effect as large as 9 at 25°C (*51*). For the oxidation of propan-2-ol by $[Ru^{IV}(trpy)(diamine)(O)]^{2+}$, the rate constants differ by a factor of about 2 despite the $E^0[Ru^{IV}/Ru^{III}]$ values range over 200 mV (*29*). The effect of hydrophobic and steric properties of the pnictogen ligands in $[Ru(bpy)_2(PnR_3)(O)](ClO_4)_2$ on their oxidative reactivity has also been studied (*53*). A mechanism involving a preassociation of target alcohol and coordinated phosphine ligand prior to hydride transfer is proposed (*53*). Recently, a molecular orbital analysis of the interaction between $[RuN_5(O)]^{2+}$ and methanol oxidation suggests that a pathway that involves precoordination of the alcohol to the metal is competitive with one that involves C—H activation by the oxo alone (*54*).

Oxidation of alkenes by $[Ru^{IV}(trpy)(diamine)(O)]^{2+}$ and $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ has been investigated (*28, 29, 43, 55*). Both epoxidation and oxidative cleavage of C=C bonds have been observed and the reaction with *cis*-stilbene is not stereorententive. The oxidation has been investigated in acetonitrile and is found to obey second-order kinetics: rate = $k_2[Ru^{IV}{=}O][alkene]$. For the oxidation by $[Ru^{IV}(trpy)(6,6'\text{-}Cl_2bpy)(O)]^{2+}$, the rate constants respond to both electronic and steric properties of alkenes (*29*). A charge-transfer mechanism alone is insufficient to explain the experimental finding. For example, with the exception of *p*-methoxystyrene, the dependence of log k_2 on the substitution constants (σ^+) of *para*-substituted styrenes is small (*29*). Changing the $E^0[Ru^{IV}/Ru^{III}]$ of $[Ru^{IV}(trpy)(diamine)(O)]^{2+}$ by over 200 mV has only a slight effect on the rate constants of styrene oxidation (see Section II,C,1,c, Table VIII). It has been suggested that the oxidation involves preassociation of Ru=O and alkene as evidenced by the large and negative $\Delta S^\ddagger$ values (*29*). Catalytic epoxidation of alkenes by PhIO has been achieved with $[Ru^{IV}(trpy)(BiQN)(O)]^{2+}$ as catalyst and by carrying out the reaction in dichloromethane (*44*). The kinetics of oxidation of phenol by $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ has been investigated (*56*). A mechanism involving an electrophilic attack of Ru=O on the aromatic ring is proposed.

Two reports on the kinetics of the reduction of Ru(IV)=O by inorganic complexes have appeared. The reaction between $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and $[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ to form two equivalents of $[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ occurs with a solvent isotope effect (k_{H_2O}/k_{D_2O}) of 16.1 ± 0.2 (*57*). A pathway involving the simultaneous transfer of a proton and an electron from $Ru^{II}{—}OH_2$ to $Ru^{IV}{=}O$ is suggested. Reduction of $[Ru^{IV}(N_2O_2)(O)(OH_2)]^{2+}$ to $[Ru^{III}(N_2O_2)(OH)(OH_2)]^{2+}$ by *cis*-$[Ru^{II}(NH_3)_4(isn)_2]^{2+}$ (isn = isonicotinamide) has been shown to involve prior protonation with *trans*-$[\mathrm{Ru^{IV}(N_2O_2)(OH)(OH_2)}]^{3+}$ as the reactive intermediate (*58*). The self-exchange rate constant of the *trans*-$[\mathrm{Ru(N_2O_2)(OH)(OH_2)}]^{3+/2+}$ couple is 3.1×10^{-4} $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$. The very small self-exchange rate constant has been attributed to the large reorganization energy required for the reduction of Ru(IV) to Ru(III) (*58*).

The reactivities of $[\mathrm{Ru^{IV}(14TMC)(O)(X)}]^{n+}$ and its related 15TMC, 16TMC, and $\mathrm{CRMe_3}$ analogs with organic substrates have also been examined (*30, 32*). In contrast, these macrocyclic Ru(IV)=O complexes have been shown to be weak oxidants., No reaction was observed with alkenes at room temperature. However, benzyl alcohol was oxidized to benzaldehyde. The lack of epoxidizing ability, in contrast to the system with polypyridyl ligands has been attributed to the lower E^0 values in the tertiary amine system (*30*). In contrast, $[\mathrm{Ru^{IV}(N_2O_2)(O)(H_2O)}](\mathrm{ClO_4})_2$, having a higher E^0, is capable of catalyzing the oxidation of norbornylene, styrene, and cyclooctene by PhIO (*46*).

The electrochemical behavior of oxoruthenium(IV) complexes has been extensively investigated. In general, the $\mathrm{Ru^{III}{-}OH/Ru^{II}{-}OH_2}$ couple is reversible, whereas the reversibility of the $\mathrm{Ru^{IV}{=}O/Ru^{III}{-}OH_2}$ or $\mathrm{Ru^{IV}{=}O/Ru^{III}{-}OH}$ couple is strongly affected by the pretreatment of the electrode (*59, 60*). A reversible $\mathrm{Ru^{IV}{=}O/Ru^{III}{-}OH_2}$ couple was observed when pyrolytic graphite or activated glassy carbon was used as the working electrode (*26, 28, 29, 59*). The E^0 values of the $\mathrm{Ru^{IV}{=}O/Ru^{III}{-}OH_2}$ and $\mathrm{Ru^{IV}{=}O/Ru^{III}{-}OH}$ couples shift cathodically with increase in pH in a manner predicted by the Nernst equation for a two-proton–one-electron and a one-proton–one-electron transfer couple, respectively. For $[\mathrm{Ru^{IV}(bpy)_2(py)(O)}]^{2+}$, which is a representative example, a Latimer diagram summarizing the aqueous acid–base and redox chemistry is shown in Scheme 1.

In 1 *M* $\mathrm{HClO_4}$; vs SCE

$$\begin{tikzcd}
\mathrm{Ru(bpy)_2(py)(O)^{2+}} \arrow[r, "+0.99\mathrm{V}"] & \mathrm{Ru(bpy)_2(py)(OH_2)^{3+}} \arrow[r, "+0.78\mathrm{V}"] \arrow[d, shift right, "\mathrm{p}K_a=0.85"'] & \mathrm{Ru(bpy)_2(py)(OH_2)^{2+}} \arrow[d, shift right, "\mathrm{p}K_a=10.26"'] \\
& \mathrm{Ru(bpy)_2(py)(OH)^{2+}} \arrow[u, shift right] & \mathrm{Ru(bpy)_2(py)(OH)^{+}} \arrow[u, shift right]
\end{tikzcd}$$

pH 7; 1 *M* $\mathrm{LiClO_4}$; vs SCE

$$\begin{tikzcd}
\mathrm{Ru^{IV}(bpy)_2(py)(O)^{2+}} \arrow[r, "+0.53\mathrm{V}"] \arrow[rr, dash, bend left, "+0.47\ \mathrm{V}"] & \mathrm{Ru(bpy)_2(py)(OH)^{2+}} \arrow[r, "+0.42\mathrm{V}"] & \mathrm{Ru(bpy)_2(py)(OH_2)^{2+}}
\end{tikzcd}$$

SCHEME 1

The electrochemical behavior of $[Ru(trpy)(bpy)(OH_2)]^{2+}$ in aqueous solution and when incorporated in Nafion coatings has been studied in detail by McHatton and Anson (*59*). The effect of ligand variation on the redox potentials of other Ru(IV)=O systems is summarized in Table II. For $[Ru(trpy)(diamine)(O)]^{2+}$, the E^0 values fall in the order of L: TMEA < 4,4′-$(MeO)_2$bpy < bpy < 6,6′-Cl_2-bpy, which is the order of the relative σ-donor strength of L.

The electrochemical behavior of ruthenium(IV) oxo complexes of tertiary amine has also been extensively studied. For the $[Ru^{IV}(L)(O)(OH_2)]^{2+}/[Ru^{III}(L)(OH)(OH_2)]^{2+}$ couples, the ring size of the macrocycle L has very little effect on E^0. However, replacement of a tertiary nitrogen donor by a pyridyl group leads to an increase in E^0.

TABLE II

SUMMARY OF FORMAL POTENTIALS FOR SELECTED RUTHENIUM AND OSMIUM OXO COMPLEXES

Ruthenium(VI)
Electrode reaction:
At pH 1.0, $[Ru^{VI}(O)_2]^{2+} + 2H^+ + 2e^- \rightarrow [Ru^{IV}(O)(OH_2)]^{2+}$

Complex	$E°$ (V vs SCE)	**Ref.**
trans-$[Ru^{VI}(14TMC)(O)_2](ClO_4)_2$	0.66	*30*
trans-$[Ru^{VI}(15TMC)(O)_2](ClO_4)_2$	0.67	*30*
trans-$[Ru^{VI}(16TMC)(O)_2](ClO_4)_2$	0.66	*30*
trans-$[Ru^{VI}(TMEA)_2(O)_2](ClO_4)_2$	0.67	*30*
trans-$[Ru^{VI}(CRMe_3)(O)_2](ClO_4)_2$	0.76	*32*
trans-$[Ru^{VI}(pytn)(O)_2](ClO_4)_2$	0.89	*203*
trans-$[Ru^{VI}(N_2O_2)(O)_2](ClO_4)_2$	0.92	*46*
trans-$[Ru^{VI}(bpy)_2(O)_2](ClO_4)_2$	1.01	*193*
trans-$[Ru^{VI}(5,5'Me_2bpy)_2(O)_2](ClO_4)_2$	1.00	*192*
cis-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2(O)_2](ClO_4)_2$	1.16	*198, 200*

Ruthenium(VI)
Electrode reaction:
At pH 1.0, $[Ru^{VI}(O)_2]^{2+} + H^+ + e^- \rightarrow [Ru^{V}(O)(OH)]^{2+}$

Complex	$E°$ (V vs SCE)	**Ref.**
cis-$[Ru^{VI}(bpy)_2(O)_2](ClO_4)_2$	1.23	*132, 133*
cis-$[Ru^{VI}(Tet\text{-}Me_6)(O)_2](ClO_4)_2$	0.80	*134*

(*continued*)

TABLE II (*Continued*)

Ruthenium(V)
Electrode reaction:
$[Ru^{V}(O)X]^{2+} + e^{-} \rightarrow [Ru^{IV}(O)X]^{+}$

Complex	$E°$	Ref.
	(V vs SCE)	
$[Ru^{V}(N_4O)(O)](ClO_4)_2$	0.98 (pH 2.0)	*45*
$[Ru^{V}(pyen)(O)Cl]^{2+}$	1.29 (pH 1.0)	*140*
	(V vs $Cp_2Fe^{+/0}$)	
trans-$[Ru^{V}(14TMC)(O)(NCO)]^{2+}$	0.89 (MeCN)	*30*
trans-$[Ru^{V}(14TMC)(O)Cl]^{2+}$	1.10 (MeCN)	*30*
trans-$[Ru^{V}(14TMC)(O)(N_3)]^{2+}$	0.72 (MeCN)	*30*
trans-$[Ru^{V}(15TMC)(O)Cl]^{2+}$	1.10 (MeCN)	*30*
trans-$[Ru^{V}(CRMe_3)(O)(NCO)]^{2+}$	0.96 (MeCN)	*32*
trans-$[Ru^{V}(TMEA)_2(O)Cl]^{2+}$	1.06 (MeCN)	*30*
	(V vs $Ag/AgNO_3$)	
trans-$[Ru^{V}(py)_4(O)Cl]^{2+}$	1.39 (MeCN)	*39*

Ruthenium(IV)
Electrode reaction:
$[Ru^{IV}(O)]^{2+} + H^{+} + e^{-} \rightarrow [Ru^{III}(OH)]^{2+}$

Complex	$E°$	Ref.
	(V vs SCE)	
$[Ru^{IV}(trpy)(bpy)(O)](ClO_4)_2$	0.62 (pH 7.0)	*36*
$[Ru^{IV}(trpy)(4,4'\text{-}Me_2bpy)(O)](ClO_4)_2$	0.55 (pH 7.0)	*36*
cis-$[Ru^{IV}(trpy)(pic)(O)](ClO_4)_2$	0.56 (pH 7.0)	*37*
$[Ru^{IV}(trpy)(pic)(O)](ClO_4)_2$	0.45 (pH 7.0)	*37*
$[Ru^{IV}(trpy)(TMEA)(O)](ClO_4)_2$	0.93 (pH 1.0)	*28*
$[Ru^{IV}(trpy)(6,6'\text{-}Cl_2bpy)(O)](ClO_4)_2$	1.13 (pH 1.0)	*29*
$[Ru^{IV}(bpy)_2(PEt_3)(O)]^{2+}$	0.97 (pH 2.0)	*42*
$[Ru^{IV}(bpy)_2(SbPh_3)(O)]^{2+}$	1.10 (pH 2.0)	*42*
$[Ru^{IV}(bpy)_2(PMe_3)(O)]^{2+}$	1.10 (pH 2.0)	*42*
$[Ru^{IV}(bpy)_2(P^{i}Pr_3)(O)]^{2+}$	0.98 (pH 2.0)	*42*
$[Ru^{IV}(bpy)_2(PPh_3)(O)]^{2+}$	1.06 (pH 2.0)	*42*
$[Ru^{IV}(bpy)_2(AsPh_3)(O)]^{2+}$	0.97 (pH 2.0)	*42*
$[Ru^{IV}(bpy)_2(SbPh_3)(O)]^{2+}$	1.10 (pH 2.0)	*42*
$[Ru^{IV}(bpy)_2(PCy_3)(O)]^{2+}$	0.99 (pH 2.0)	*42*
$[Ru^{IV}(bpy)_2(P(p\text{-}CF_3C_6H_4)_3)(O)]^{2+}$	1.23 (pH 2.0)	*42*
$[Ru^{IV}(bpy)(biq)(PEt_3)(O)]^{2+}$	0.91 (pH 1.97)	*27*
$[Ru^{IV}(biq)_2(PEt_3)(O)]^{2+}$	0.91 (pH 1.97)	*27*
$[Ru^{IV}(bpy)(biq)(PPh_3)(O)]^{2+}$	1.0 (pH 2.0)	*27*
$[Ru^{IV}(tpm)(bpy)(O)](ClO_4)_2$	0.71 (pH 7.0)	*37*
$[Ru^{IV}(tpm)(4,4'\text{-}Me_2bpy)(O)](ClO_4)_2$	0.66 (pH 7.0)	*37*

TABLE II (*Continued*)

Complex	E°	Ref.
$[Ru^{IV}(tpm)(phen)(O)](ClO_4)_2$	0.71 (pH 7.0)	*37*
$[Ru^{IV}(14TMC)(O)(OH_2)]^{2+}$	0.36 (pH 1.0)	*30*
$[Ru^{IV}(15TMC)(O)(OH_2)]^{2+}$	0.34 (pH 1.0)	*30*
$[Ru^{IV}(16TMC)(O)(OH_2)]^{2+}$	0.33 (pH 1.0)	*30*
$[Ru^{IV}(CRMe_3)(O)(OH_2)]^{2+}$	0.52 (pH 1.1)	*32*
$[Ru^{IV}(N_2O_2)(O)(H_2O)](ClO_4)_2$	0.62 (pH 1.0)	*46*

Osmium(VI)
Electrode reaction:
$[Os^{VI}(O)_2]^{2+} + e^- \rightarrow [Os^{V}(O)_2]^+$

Complex	E°	Ref.
	(V vs $Cp_2Fe^{+/0}$, CH_2Cl_2)	
cis-$[Os^{VI}(O)_2(S_2O_3)_2]Na_2$	−1.10	*256*
	(V vs $Cp_2Fe^{+/0}$, CH_3CN)	
trans-$[Os^{VI}(O)_2(CN)_4](Ph_4As)_2$	−1.52	*175*
	(V vs $Ag/AgNO_3$, CH_3CN)	
trans-$[Os^{VI}(3\text{-}t\text{-Bu-saltmen})(O)_2]$	−1.38	*229*

Osmium(VI)
Electrode reaction:
$[Os^{VI}(O)_2]^{2+} + H^+ + e^- \rightarrow [Os^{V}(O)(OH)]^{2+}$

Complex	E°	Ref.
	(V vs SCE)	
cis-$[Os^{VI}(O)_2(bpy)_2]^{2+}$	0.81 (pH 1.0)	*74*

Osmium(VI)
Electrode reaction:
$[Os^{VI}(O)_2]^{2+} + 3H^+ + 3e^- \rightarrow [Os^{III}(OH)(OH_2)]^{2+}$

Complex	E°	Ref.
	(V vs SCE)	
trans-$[Os^{VI}(O)_2(bpy)_2]^{2+}$	0.51 (pH 1.0)	*74*
trans-$[Os^{VI}(trpy)(O)_2(OH)]^+$	0.44 (pH 1.0)	*213*
trans-$[Os^{VI}(O)_2(14TMC)](ClO_4)_2$	0.04 (pH 1.0)	*75*
trans-$[Os^{VI}(O)_2(15TMC)](ClO_4)_2$	0.05 (pH 1.0)	*75*
trans-$[Os^{VI}(O)_2(16TMC)](ClO_4)_2$	0.05 (pH 1.0)	*75*
trans-$[Os^{VI}(O)_2(CRMe_3)](ClO_4)_2$	0.14 (pH 1.0)	*75*

The electrochemical behavior of these proton-coupled electron transfers will be discussed in Section II,C,1,c.

Other oxoruthenium(IV) complexes with nitrogen ligands are the oxo-bridged dimers, which were reported to be active electrocatalysts for chloride and water oxidation (*24*). The complex $[(bpy)_2ClRu^{III}ORu^{IV}Cl(bpy)_2](PF_6)_3$ has been isolated by the oxidation of the Ru(III)—Ru(III) complex by chlorine in dichloromethane (*61*). However, it is not stable and cannot be stored for long periods of time. Dimeric species of $[(b)_2(H_2O)Ru^{III}ORu^{IV}(OH)(b)_2]^{4+}$ (*62*) and $[(b)_2(O)Ru^{IV}ORu^{V}(O)(b)_2]^{3+}$ (*63*) have been generated in solutions by the electrochemical oxidation of the Ru(III)—Ru(III) species (b = bpy, 5,5′-$(COOH)_2$bpy). The redox potentials as a function of pH have been subjected to detailed studies (*62, 63*) (see Section II,B,1,c).

A novel tri-oxo-bridged diruthenium(IV) complex of the Ligand *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (Me_3tacn) has been described (*64*). This complex, $[(Me_3tacn)Ru^{IV}(\mu\text{-}O)_3Ru^{IV}(Me_3tacn)]^{2+}$, is prepared by the oxidation of its $Ru_2{}^{III}$ precursor and has a temperature-dependent magnetic moment with $\mu_{eff} = 2.26\ \mu_B$ per binuclear unit at 298 K. The X-ray structure reveals a Ru—Ru distance of 2.363(2) Å, consistent with a bond order of 2. The measured Ru—O(bridge) distances range from 1.918(7) to 1.937(9) Å. Interestingly, this complex undergoes a reversible one-electron oxidation (E^0 = 1.05 V vs $Cp_2Fe^{+/0}$) in acetonitrile to give a novel green mixed-valence Ru^{IV}—Ru^{V} species, $[(Me_3tacn)Ru^{IV}(\mu\text{-}O)_3Ru^{V}(Me_3tacn)]^{3+}$.

"Ruthenium red," an intensely red species produced on air oxidation of a solution of $RuCl_3 \cdot 3H_2O$ in aqueous ammonia, is an oxo-bridged trimer, $[Ru_3O_2(NH_3)_{14}]Cl_6$. The X-ray crystal structure of the thiosulfate salt showed a linear $[RuORuORu]^{6+}$ system with octahedral arrangement about Ru (*14, 65*). The μ_{eff} of ruthenium red has been measured to be 0.77 μ_B. Mössbauer spectral studies indicate that discrete oxidation states are present in ruthenium red, Ru^{III}—ORu^{IV}—Ru^{III}. Oxidation of ruthenium red with H_2O_2, HNO_3, or Ce^{4+} gives "ruthenium brown," $[Ru_3O_2(NH_3)_{14}]^{7+}$. A μ_{eff} value of 1.13 μ_B was reported for ruthenium brown (*14*). A linear Ru—O—Ru—O—Ru backbone is also present in the ruthenium brown system, as suggested by vibrational, resonance Raman, as well as electronic spectral data. Mössbauer spectral studies suggest the presence of Ru^{IV}—ORu^{III}—ORu^{IV} discrete oxidation states in ruthenium brown (*14*).

The bpy analog of ruthenium red, $[(bpy)_2(H_2O)Ru^{III}ORu^{IV}(bpy)_2ORu^{III}(OH_2)(bpy)_2]^{6+}$, has been synthesized and characterized by XPS measurements (*66*). Its optical spectrum in 0.1 *M* acid displays an intense transition band at 653 nm ($\varepsilon_{max} \simeq 1.05 \times 10^5\ M^{-1}\ cm^{-1}$).

With porphyrin ligands, the first oxoruthenium(IV) species, $[Ru^{IV}(TMP)(O)]$, was synthesized by the stoichiometric reduction of $[Ru^{VI}(TMP)(O)_2]$ with PPh_3 (*33*). However, this Ru(IV) complex, which was characterized by magnetic susceptibility measurement ($\mu_{eff} = 2.4\ \mu_B$) and ^1H NMR spectroscopy, was found to be unstable toward disproportionation to Ru(II) and Ru(VI). Other monomeric ruthenium(IV) complexes of nonsterically bulky porphyrins, formulated as either $[Ru^{IV}(P)(O)(ROH)]$ or $[Ru^{IV}(P)(OH)_2]$ (P = porphyrin dianion), have been reported by Che and co-workers (*67, 68*). The X-ray crystal structure of $[Ru^{IV}(TMP)(OH)(OEt)]$ has also been determined (*69*). The Ru—OH and Ru—OEt bonds are in disorder and the average Ru—O distance is 1.928(9) Å. The success of the synthesis of monomeric species was proposed to depend on the solvent employed. Weakly coordinating solvents such as ethanol were thought to occupy the vacant coordination site of the $[Ru^{IV}(P)(O)]$ intermediate, thus inhibiting the μ-oxo dimerization process that leads to the formation of $[Ru^{IV}(P)(OH)]_2O$ (*67, 68*). The complex $[Ru^{IV}(P)(O)(ROH)]$ or $[Ru^{IV}(P)(OH)_2]$ has a measured μ_{eff} of 3.1 μ_B, consistent with the $(d_{xy})^2(d_{yz})^1(d_{zx})^1$ electronic configuration.

The complex $[Ru^{IV}(OEP)(O)(EtOH)]$ has been shown to react with olefins to give epoxides in degassed CH_2Cl_2/py solution; the final ruthenium product has been identified to be $[Ru^{II}(OEP)(py)_2]$ (*67*). The cyclic voltammogram of $[Ru^{IV}(OEP)(O)(EtOH)]$ in CH_2Cl_2/py displays a reversible reduction couple at -0.86 V and an irreversible oxidative wave at 0.6 V vs $Cp_2Fe^{+/0}$. The reduction has been assigned to the Ru(IV/III) couple (*69*).

Dimeric μ-oxo-Ru(IV) porphyrins, $[Ru^{IV}(P)(OH)]_2O$, are the usual product formed by the oxidation of $[Ru^{II}(P)(CO)]$ with *tert*-butylhydroperoxide, or oxidation of $[Ru(P)]_2$ with O_2 in the presence of trace amount of H_2O (P = OEP, TPP) (*70–72*). An X-ray structural study of $[Ru^{IV}(OEP)(OH)]_2O$ by Masuda and co-workers shows a linear Ru—O—Ru backbone with Ru—O(bridge) = 1.847 Å with a staggered conformation of the porphyrin rings (*70*). A range of related dimeric Ru^{IV} species $[Ru(P)(X)]_2O$ (P = OEP, TPP, TPr^nP; X = Cl^-, Br^-, OAc^-, CF_3COO^-, HSO_4^-, MeO^-, EtO^-, 2-HO-$C_6H_4O^-$, 4-HO-$C_6H_4O^-$) have also been prepared by Collman and co-workers (*72*). The structures of $[Ru(OEP)Cl]_2O$ and $[Ru(TPP)(OR)]_2O$ (OR = 4-OC_6H_4Me) have also been established by X-ray crystallography ($[Ru(OEP)Cl]_2O$, Ru—O(bridge) = 1.793 Å; $[Ru(TPP)(OR)]_2O$, Ru—O(bridge) = 1.789 Å) (*72*).

No osmium(IV) oxo species of any type has yet been isolated or characterized. The osmium(IV) oxo species were reported only as intermediates in electrochemical studies. The complex $[Os^{IV}(trpy)(bpy)(O)]^{2+}$ has been generated by the electrochemical oxidation of

$[Os^{II}(trpy)(bpy)(OH_2)]^{2+}$ (*73*). As in the case of ruthenium, pH-dependent $Os^{IV}{=}O/Os^{III}{-}OH_2$ and $Os^{IV}{=}O/Os^{III}{-}OH$ couples were observed. Interestingly, the E^0 of the $[Os^{IV}(trpy)(bpy)(O)]^{2+}/[Os^{III}(trpy)(bpy)(OH)]^{2+}$ couple, which is 0.41 V vs SSCE at pH 7, is only about 200 mV smaller than that for the related ruthenium system under similar conditions. Electrochemical oxidation of *cis*-$[Os(bpy)_2(OH_2)_2]^{2+}$ via a series of sequential one-electron oxidations to $[Os^{IV}(bpy)_2(O)(OH_2)]^{2+}$ has also been reported (*74*).

trans-Dioxoosmium(IV) complexes of macrocyclic tertiary amine ligands have also been reported to be generated in the cyclic voltammetric scans of *trans*-$[Os^{VI}(L)(O)_2]^{2+}$ (L = 14TMC, 15TMC, 16TMC, $CRMe_3$) in acetonitrile (*75*) (see Section II,C,1,c):

$$trans\text{-}[Os^{VI}(L)(O)_2]^{2+} + e^- \rightarrow trans\text{-}[Os^{V}(L)(O)_2]^{+}$$

$$trans\text{-}[Os^{V}(L)(O)_2]^{+} + e^- \rightarrow trans\text{-}[Os^{IV}(L)(O)_2]$$

The observed reversibility of the $Os^{V/IV}$ couple suggests that *trans*-$[Os^{IV}(L)(O)_2]$ is at least stable in fluid solution on the time scale of cyclic voltammetric experiments. These *trans*-$[Os^{IV}(L)(O)_2]$ complexes should be powerful reductants with E^0 of the *trans*-$[Os(L)(O)_2]^{+/0}$ couples being −1.64, −1.70, −1.66, and −1.48 V vs $Cp_2Fe^{+/0}$ for L = 14TMC, 15TMC, 16TMC, and $CRMe_3$, respectively.

A number of μ-oxo-osmium(IV) complexes have been reported. Mixed-valent $[(OH_2)(bpy)_2Os^{III}{-}O{-}Os^{IV}(bpy)_2(OH)]^{4+}$ and $[(trpy)(bpy){-}Os^{III}{-}O{-}Os^{IV}(bpy)(trpy)]^{5+}$ have been isolated (*76*).

A μ-oxo-bridged $K_2[Os_2O(\eta^4\text{-chbaEt})(OPPh_3)_2]$ complex, prepared by the reaction of $K_2[Os(O)_2(chbaEt)]$ with PPh_3, has also been structurally characterized (*77*). As in $Cs_4[Os_2OCl_{10}]$ (*21*), the equatorial ligands are eclipsed, but the Os—O—Os bridge is not quite linear [Os—O—Os angle = 175.5°, Os—O(bridge) = 1.795 Å]. Another μ-oxo complex containing a bent bridge is $[Os_2O(OAc)_2Cl_4(PPh_3)_2]$, prepared from the reaction of *trans*-$[Os(O)_2Cl_2(PPh_3)_2]$ and acetic anhydride. X-ray structural studies on $[Os_2O(OAc)_2Cl_4(PPh_3)_2]\cdot Et_2O$ showed that the Os—O—Os moiety is spanned by two bridging acetato ligands [Os—O—Os angle = 140.2(4), Os—O(bridge) = 1.830(10) Å] (*78*). The complex has been shown to be diamagnetic with a Os···Os distance of 3.440(2) Å. The cyclic voltammogram showed a reversible one-electron reduction, and the purple paramagnetic $Os^{III}{-}Os^{IV}$ complex anion, $[Os_2O(OAc)_2Cl_4(PPh_3)_2]^-$, has been isolated. Other $[Os_2O(OCOR)_2Cl_4(PR_3')_2]$ complexes (R = Me, Et; X = Cl, Br; PR_3' = PPh_3 or PEt_2Ph) have been studied similarly (*78*). A linear μ-oxo-diosmium(IV) molecule bridged by two dppm ligands, $[Os_2(\mu\text{-}O)(\mu\text{-dppm})_2Cl_6]$, has been prepared by reacting $OsCl_3$ with dppm (*79*). It has a linear Os—O—Os unit with an Os—O bond distance of 1.792(1) Å. Interestingly, it undergoes a reversible one-electron oxidation to give formally an Os^{IV}—O—Os^{V} complex, $[Os_2(\mu\text{-}O)(\mu\text{-dppm})_2Cl_6]^+$.

A number of μ-oxo-osmium(IV) porphyrin complexes have been prepared by the reaction of $[Os^{II}(OEP)(CO)(MeOH)]$ with air and 2,3-dimethylindole in dichloromethane (*80*). Cyclic voltammetric studies show that $[Os_2O(OEP)_2(OMe)_2]$ can undergo reduction to give an Os^{IV}—Os^{III} dimer. The X-ray crystal structure of $[Os(OEP)(OMe)]_2O$ revealed a linear Os—O—Os backbone with Os^{IV}—O and Os^{IV}—OCH_3 distances of 1.808(3) and 1.997(29) Å, respectively (*81*).

d. Group VI Ligands. No ruthenium(IV) and osmium(IV) oxo complexes with this group of ligands have been reported.

2. *Nitrido Complexes*

No mononuclear nitrido complexes of Ru(IV) and Os(IV) have yet been isolated.

Reaction of $[RuCl_5(NO)]^{2-}$ with $SnCl_2$ or HCHO yielded $[Ru_2NCl_8(H_2O)_2]^{3-}$ (*82, 83*). The X-ray crystal structures of $K_3[Ru_2NCl_8(H_2O)_2]$ (*84*) and $(NH_4)_3[Ru_2NCl_8(H_2O)_2]$ (*85*) have been established. The anions in both salts are isostructural with d(Ru—N) = 1.72 Å, $d(Ru—O(OH_2))$ = 2.18 Å, ∠O—Ru—N = 179.7°, indicating a centrosymmetric structure. The O—Ru—N—Ru—O skeleton is linear with the chlorine atoms in an eclipsed configuration. The osmium analog $[Os_2NCl_8(H_2O)_2]^{3-}$ has also been obtained in low yield by refluxing an aqueous solution of $K_3[Os(NH_2SO_3)Cl_5]$, possibly with $K_5[Os_2NCl_{10}]$ as a minor product (*86*). A similar structure has been proposed for the osmium analog based on the considerable similarities in the Raman and IR spectra of the ruthenium and osmium complexes (*83*). The short Ru—N distance indicated a considerable multiple bonding character for the Ru—N linkage, possibly being considered as $[(H_2O)Cl_4Ru{=}N{=}RuCl_4(H_2O)]^{3-}$.

A range of other substituted nitrido dimers have also been reported. Examples include $[Ru_2NBr_8(OH_2)_2]^{3-}$, $[Ru_2N(NCS)_8(OH_2)_2]^{3-}$, and $[Ru_2N(NO_2)_6(OH)_2(OH_2)_2]^{3-}$, which have similar structures on the basis of their vibrational spectra (*83*). The vibrational spectra of these complexes are also consistent with a linear Ru—N—Ru backbone with $\nu_{as}(Ru_2N)$ ~1000–1100 cm^{-1}. Other examples that are unusual for high oxidation state complexes are the $[Ru_2NX_8(CO)_2]^{3-}$ (X = Cl, Br) and the $[Ru_2N(CN)_{10}]^{5-}$ complexes (*87*), formed from the reaction of $[Ru_2NCl_8(OH_2)_2]^{3-}$ in concentrated HX with CO and KCN, respectively.

This unusual formation of the carbonyl and cyanide complexes of Ru(IV) has been rationalized on the basis of the Ru—N multiple bonding character, which would render the electron density on ruthenium higher than normally found, and hence more readily delocalized onto the π-acceptor ligands. Cationic complexes such as $[Ru_2NX_2(NH_3)_8]^{3+}$ (X = Cl, Br, NO_3) and $[Ru_2NX_3(NH_3)_6(OH_2)]^{2+}$ (X = Cl, NCS, N_3) (*83*) have also been reported. The X-ray crystal structure of $[Ru_2N(en)_5]^{5+}$, prepared from the prolonged treatment of $[Ru_2NCl_8(OH_2)_2]^{3-}$ with en, shows a bridging en ligand with Ru—N(nitride) = 1.742 Å and ∠Ru—N—Ru = 174.6° (*88*).

Osmium(IV) nitrido dimers of $[Os_2N(NH_3)_8X_2]^{3+}$ (X = Cl, Br, I, NCS, N_3, NO_3) are also known (*83*). The complex $[Os_2N(NH_3)_8Cl_2]Cl_3$ has been obtained by heating $Na_2[OsCl_6]$ with aqueous ammonia under pressure (*89*) or from $K_3[Os_2NCl_8(OH_2)_2]$ and ammonia (*83*). Metathesis in cold aqueous solution converts $[Os_2N(NH_3)_8Cl_2]Cl_3$ into $[Os_2N(NH_3)_8Cl_2]X_3$ (X = Br, I, NO_3, N_3, NCS), and on heating $[Os_2N(NH_3)_8X_2]X_3$ are produced (*83*). Vibrational spectra suggest that all contain linear Os—N—Os units. A reversible Os^{V}—N—Os^{IV}/Os^{IV}—N—Os^{IV} couple at 0.90 V vs SCE has been observed for $[Os_2(N)(NH_3)_7Cl_3]Cl_2$. Dithiocarbamato complexes, $[Os_2N(S_2CNR_2)_5]$, have been prepared from $OsCl_3$ and $Na[R_2dtc]$ (R = Me, Et). The X-ray structure shows an unusual nonlinear Os—N—Os arrangement with ∠Os—N—Os = 164.6(18)° and d(Os—N) = 1.76(3) Å (*90*). The slightly bent, symmetric nitrido bridge is a result of the short "bite" of the bridging dithiocarbamate ligand. Electrochemical studies of $[Os_2N(S_2CNEt_2)_5]$ in MeCN revealed a well-defined reversible oxidation couple at $E_{1/2}$ = 0.43 V vs SCE assignable to the oxidation of Os^{IV}—N—Os^{IV} to Os^{IV}—N—Os^{V} (*91*). Reaction of $(NH_4)_2[OsCl_6]$ with $N_2H_4 \cdot H_2O$ under refluxing conditions gave the golden yellow complex $[Os_2N(NH_3)_{10}]Cl_5$, which showed a $\nu(Os{\equiv}N{\equiv}Os)$ stretch at 1100 cm^{-1} (*92*).

All these complexes of Ru(IV) and Os(IV) are diamagnetic. A molecular orbital scheme for the bonding in $[Os_2OCl_{10}]^{4-}$ has been proposed to explain a similar bonding picture in these μ-nitrido complexes, with p_π–d_π interactions for $2p$ orbitals on N^{3-} and $5d_{xy}$, $5d_{yz}$ orbitals on osmium ($4d_{xz}$, $4d_{yz}$ orbitals on ruthenium) giving rise to the observed diamagnetism (*93*).

Trinuclear species have also been reported. A blue-black ruthenium violet, proposed to be $[Ru_3N_2(NH_3)_8(OH)(OH_2)_5]^{5+}$ (μ_{eff} = 0.8 μ_B), has been isolated as a side-product in the preparation of ruthenium red from aqueous ammoniacal solution of $RuCl_3$ (*94*). Reaction of $(NH_4)_2[OsCl_6]$ with ammonia gives a diamagnetic purple species, osmium violet, proposed to be $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$. The XPS data on osmium violet support the presence of Os(IV) (*94*). A cyano analog, $[Os_3N_2(CN)_{10}(OH_2)_4]^{4-}$, was also reported (*94, 95*). However, no X-ray crystal structure on these complexes has yet been established. Vibrational spectral data suggest that the Os_3N_2 unit has considerable multiple bond character. The bonding has been rationalized using the molecular orbital scheme for the trimeric ruthenium oxo-bridged system (*96, 97*).

3. *Imido Complexes*

No mononuclear imido complexes of Ru(IV) have yet been isolated. The recently reported imido-bridged dimer $[Ru(\eta\text{-}C_6H_6)(N\text{-}2,6\text{-}Pr_2{}^iC_6H_3)]2_2$ has ruthenium in an oxidation state of +II (*98*).

It has been argued that Ru(IV) plays an important role in the facile oxidation of coordinated amines. A Ru(IV) imido species, $[Ru(sar\text{-}H)]^{3+}$, characterized by UV–VIS spectroscopy, was generated by two-electron oxidation of $[Ru(sar)]^{2+}$ (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) (*99*). This species was short-lived and rapidly transformed into a Ru(II) imine species. The E^0 of the $[Ru(sar\text{-}H)]^{3+}/[Ru(sar)]^{2+}$ couple was found to obey $E = 0.355 + (0.059/2)\log[H^+]$ V.

The X-ray crystal structure of [*cis*-1,2-ethanediaminebis(1,2-ethanediaminato(1-)]osmium(IV) dibromide has been determined (*100*). The short Os—N(aminate) bonds (1.90 Å) are attributed to the bonding interaction between the filled p_π orbitals of the ligands and the empty *d* orbitals on Os(IV).

Meyer and co-workers (*101*) have described the electrogeneration of $[(trpy)(bpy)Os^{IV}{=}NH]^{2+}$ from $[(trpy)(bpy)Os^{II}{-}NH_3]^{2+}$. This Os(IV) imido species was detected in the cyclic voltammetric time scale and reacted rapidly with secondary amines to give osmium(II) nitrosamines.

The first X-ray crystal structure of Os(IV) imido complex is $Os(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_2(PMe_2Ph)_2$ (Fig. 3), prepared by the reaction of $[Os(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3]$ with PMe_2Ph. It is a square-planar complex in which there is a crystallographic inversion center. The Os=N distance is 1.790(6) Å and the imido ligands are virtually linear (Os—N—C angle = 177.9(5)°) (*102*).

4. *Other Complexes*

Ruthenium vinylidene and carbene complexes containing cyclopentadienyl ligands such as $[(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru{=}C{=}CH_2]^+$ are known and an excellent review describing the structures and reactivities of these classes of complexes is available (*103*). Treatment of the *N,N*′-vinyl-bridged porphyrin with $Ru_3(CO)_{12}$ yielded $(TPP)Ru\{C{=}C(p\text{-}Cl\text{-}C_6H_4)_2\}$,

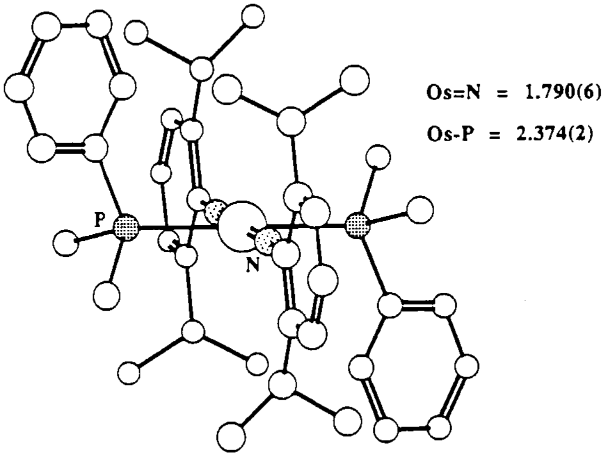


FIG. 3. A drawing of *trans*-Os(N-2,6-C_6H_3-*i*-Pr_2)$_2$(PMe_2Ph)$_2$. From Ref. (*102*).

characterized by ^1H NMR spectroscopy (*104*). If one adopts the Schrock-type formulation, such complexes have ruthenium in a formal oxidation state of +IV. Ruthenium silylene complexes such as $[(\eta^5\text{-}C_5M_5)(PMe_3)_2Ru{=}SiPh_2]^+$ have been synthesized and characterized by X-ray crystallography (Fig. 4) (*105, 106*). The measured Ru–Si distances range from 2.387(1) to 2.328(2) Å. Collman and co-workers reported the formation of Ru(TPP)(CH(CH_3)) and Ru(TPP)(CH($SiMe_3$)) by the reactions of a zero-valent metalloporphyrin dianion, K_2[Ru(TPP)], with

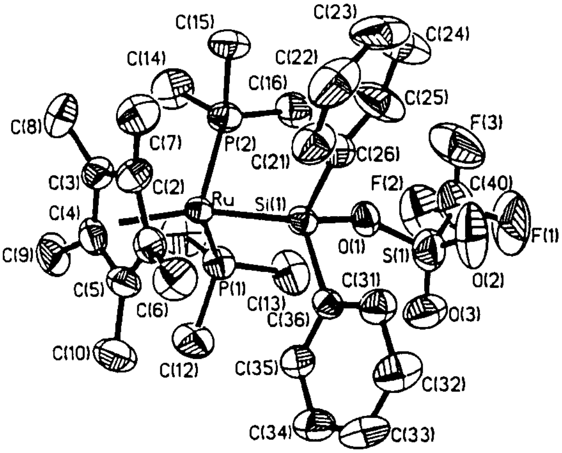


FIG. 4. ORTEP view of (η^5-C_5Me_5)(PMe_3)$_2$Ru$SiPh_2$OTf with atomic labeling scheme. From Ref. (*105*).

organic electrophiles. These complexes are diamagnetic and have been characterized by ^{1}H NMR spectroscopy (*107, 108*). With a tetraanionic bisamide ligand, a paramagnetic bluish-green [Ru^{IV}(chbae)(PPh$_3$)(py)] complex (μ_{eff} = 3.08 μ_B at 25°C) was prepared by the reaction of [Ru(PPh$_3$)$_3$Cl$_2$] with H$_4$chbae under aerobic conditions (*109*). The X-ray crystal structure revealed the Ru^{IV}—N(amide) distances to be in the range 1.987–2.044(5) Å. The reaction between [Ru(TPP)(O)$_2$] and Ph$_2$NH gave a novel bis(amido)ruthenium(IV) complex, [Ru(TPP)(NPh$_2$)$_2$], characterized by ^{1}H NMR spectroscopy (*110*). Since Ph$_2$N$^-$ can act only as a four-electron donor, [Ru(TPP)(NPh$_2$)$_2$] is diamagnetic in its ground state. The first paramagnetic Ru(IV) porphyrin that has been characterized structurally is [Ru(TPP)Br$_2$] with d(Ru—Br) = 2.425(2) Å (*111*).

Various monomeric bis(alkoxy)osmium(IV) porphyrins have been prepared by either reduction of [Os(P)(O)$_2$] or oxidation of [Os(P)(N$_2$)(THF)] in alcohol (*112–115*). Magnetic susceptibility measurements revealed a paramagnetic triplet ground state $(d_{xy})^2(d_{xz})^1(d_{yz})^1$ with μ_{eff} ranging from 2.27 to 2.60 μ_B (*112*). The X-ray crystal structures of [Os(TPP)(OR)$_2$] (R = Et, ^{i}Pr, Ph) have been determined: the RO—Os—OR axis is essentially linear and the Os—OR distances range from 1.909(4) to 1.938(2) Å (*115*). Reversible Os(V)/(IV) couples have been observed for these [Os(P)(OR)$_2$] complexes with E^0 ranging from 0.15 to 0.39 V vs Cp$_2$Fe$^{+/0}$ in CH$_2$Cl$_2$ (*112*).

The first silylene complexes of osmium porphyrin, (TTP)Os=SiR$_2$·THF, were prepared by treating K$_2$[Os(TTP)] with Cl$_2$SiR$_2$ or the reaction of [Os(TTP)]$_2$ with hexamethylsilacyclopropane (*116*). The molecular structure of (TTP)Os=SiEt$_2$·2THF is stabilized by coordination of THF to the silicon, as shown by X-ray crystallography (Fig. 5). The measured Os—Si distance of 2.325(8) Å is the shortest ever reported (*116*).

Taube and co-workers (*117*) investigated the synthesis and reactivities of [M^{IV}(Cp)$_2$X]$^+$ (M = Ru, Os; X = halide). These species behave as two-electron atom transfer donors and the self-exchange rate constants of the couples [M(Cp)$_2$X]$^+$/[M(Cp)$_2$] have been determined by ^{1}H NMR measurements.

B. OXIDATION STATE +V

1. *Oxo Complexes*

a. Oxides and Oxoanions. Oxoanions of Ru(V) are known (*14*). Reaction between RuO$_2$ and Na$_2$O$_2$ at 700°C gave a blue microcrystalline cluster species, soluble in water (*118*). This has been shown to consist

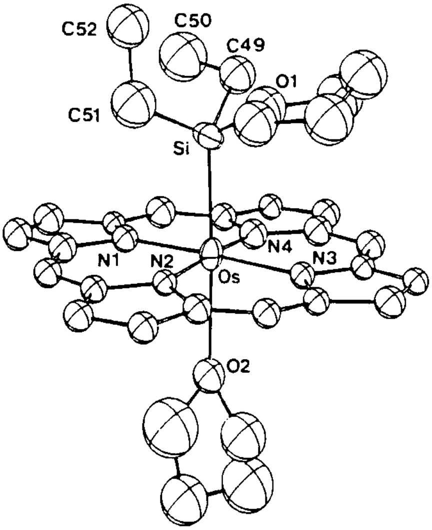


FIG. 5. Molecular structure with 50% probability thermal ellipsoids and partial atom numbering scheme for (TTP)Os=$SiEt_2$·2THF. From Ref. (*116*).

of $[Ru_4O_{16}]^{2-}$ units and has been proposed to exist in Na_3RuO_4 (*119*). The magnetic properties and the Mössbauer spectrum of Na_3RuO_4 have been studied in detail (*120*). Species of the type $Na_4Ru_2O_7$, Li_7RuO_6, and $Li_3[RuO_4]$ have also been reported (*14, 121*). Quaternary ruthenium(V) oxides of the form $Ba_3Ru_2M^{II}O_9$ (M^{II} = Ni, Mg, Cd, Ca, Sr) have also been prepared (*122, 123*). Related compounds, which include the perovskites A_2BRuO_6 (A = Ba, B = La, Pr, Nd, Sm, Eu, Gd, Dy, Bi, Y, or Yb; A = Sr, B = La, Ce, Pr, Nd, Sm, Gd, Y, or Yb), have also been prepared (*124*). The structure of Sr_2FeRuO_6 has been determined to be an orthorhombic perovskite with cell parameters of a = 5.53, b = 5.56, and c = 7.82 Å (*125*). Studies have shown that Ba_2LaRuO_6 can catalyze reactions of the type (*124*)

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

$$2CO + O_2 \rightarrow 2CO_2$$

Osmates(V) reported include $Li_3[OsO_4]$ (*126*), $Na[OsO_3]$ (*127*), $Ca_2[Os_2O_7]$ (*126, 127*), and $Li_7[OsO_6]$ (*128*). The salt $Li_7[OsO_6]$ shows a hexagonal-type lattice structure with an estimated d(Os=O) of 2.07 Å (*128*). The reported Os_2OCl_8, made from osmium metal and a 15 : 1 chlorine–oxygen mixture at 700°C, is probably $OsOCl_4$ instead (*129*).

b. Group IV Ligands. Reaction of RuO_4 with an ice-cold solution of NaCN in the presence of cesium ions gave a paramagnetic green complex, $Cs_3[RuO(CN)_4(NCO)_2]$ ($\mu_{eff} = 3.0\ \mu_B$), with bands in its IR and Raman spectra at 787 cm^{-1}, assigned as $\nu(Ru{=}O)$ absorption (*87*). Since seven-coordinate Ru(V) complexes are not known, further characterization of this species is required.

Careful oxygenation of Ru_2R_6 (R = CH_2SiMe_3, CH_2CMe_3) in toluene at $-80°C$ with nitrosobenzene yielded a red crystalline compound, confirmed as $(RuOR_3)_2$ (Fig. 6) (*130*). The IR absorption band at 908 cm^{-1} has been assigned as the Ru=O stretch. The X-ray crystal structure of $[RuO(CH_2SiMe_3)_3]_2$ has been obtained (*130*). The molecule comprises two RuO_2C_3 trigonal bipyramids in which the equator is formed from one oxo oxygen atom and two alkyl carbons, linked via oxygen bridges between one axial and one equatorial site [Ru=O 1.733(6) Å, Ru···O 2.208(6) Å, Ru—Ru 2.738(4) Å]. A similar asymmetric mode of bridging has been found in the "18-electron" osmium(VI) complex, (cyclohexane-1,2-diolato)dioxo-(quinuclidine)osmium, in which the di-μ-oxo bridge [Os=O 1.78(1) Å, Os···O 2.22(1) Å] is between two sites on each of two OsO_5N octahedra (*131*). The diamagnetism of the complex has been suggested to result from the single Ru—Ru link in contrast to the osmium complex, which dimerizes only via oxygen bridg-

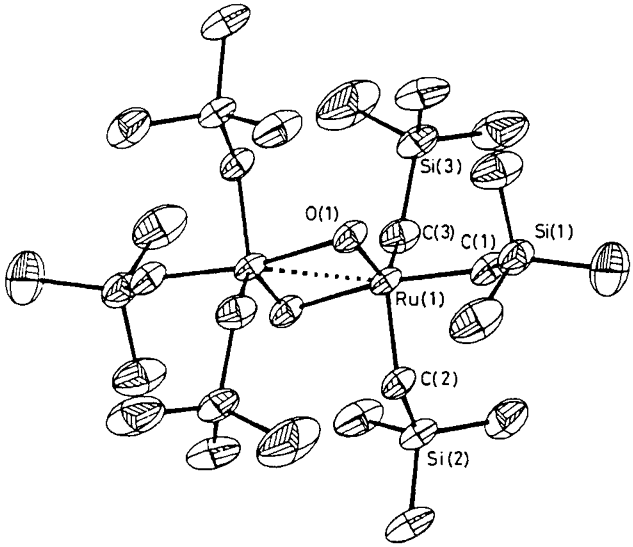
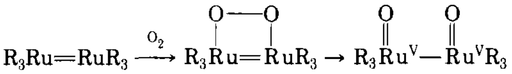


FIG. 6. Molecular structure of dioxohexakis(trimethylsilylmethyl)-diruthenium(V), $[RuO(CH_2SiMe_3)_3]_2$. From Ref. (*130*).

ing. The reaction of Ru_2R_6 with O_2 or nitrosobenzene to give the metal–metal bridged oxoruthenium(V) species is proposed as follows:



$$R_3Ru{=}RuR_3 \xrightarrow{O_2} R_3\overset{\text{O—O}}{Ru{=}Ru}R_3 \rightarrow R_3\overset{O}{\overset{\|}{Ru^V}}—\overset{O}{\overset{\|}{Ru^V}}R_3$$

$$Ru_2R_6 + 2PhNO \rightarrow Ru_2O_2R_6 + PhN{=}NPh$$

No oxo species of Os(V) with this group of ligands has been reported.

c. Group V Ligands. Ru(V) and Os(V) oxo complexes containing polypyridine ligands have been reported as intermediates in the sequential oxidation of the corresponding metal(II) aquo complexes, as well as in the sequential reduction of the corresponding metal(VI) dioxo species. Electrochemical oxidation of both *cis*- and *trans*-$[M^{II}(bpy)_2(OH_2)_2]^{2+}$ (M = Ru, Os) gave rise to a $[M^V(bpy)_2(O)_2]^+$ or $[M^V(bpy)_2(O)(OH)]^{2+}$ species, stable within the time scale of the cyclic voltammetric experiment, depending on the pH of the solution (*132, 133*). However, no isolation of $[M^V(bpy)_2(O)(OH)]^{2+}$ nor $[M^V(bpy)_2(O)_2]^+$ complexes has been reported.

With chelating tertiary amine, an air-stable *cis*-$[Ru^V(Tet\text{-}Me_6)(O)_2]ClO_4$, whose structure has been charracterized by X-ray crystallography (Fig. 7), has been isolated. This complex was prepared by electrochemical or chemical reduction of *cis*-$[Ru^{VI}(Tet\text{-}Me_6)(O)_2]^{2+}$ and has a measured μ_{eff} of 1.9 μ_B at 25°C. Only one $\nu(Ru{=}O)$ has been located; the other one probably overlaps with the ligand stretches. The two Ru=O bonds are equivalent with measured Ru=O distances of 1.751 and 1.756 Å. The O—Ru—O angle is 115.1(2)° (*134*).

A series of *trans*-$[Ru^V(L)(O)_2]^+$ complexes [L = 14TMC, 15TMC, 16TMC, $(TMEA)_2$, $CRMe_3$, *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-propylenediamine] have been prepared by electrochemical reduction of the respective *trans*-$[Ru^{VI}(L)(O)_2]^{2+}$ species in acetonitrile solution (0.1 *M* Bu_4NClO_4) under an atmosphere of argon (*30, 32*). A μ_{eff} value of 1.94 μ_B has been obtained for *trans*-$[Ru^V(14TMC)(O)_2]ClO_4$, in accord with a $(d_{xy})^2(d_\pi{}^*)^1$ ground-state electronic configuration ($d_\pi{}^* = d_{xz}, d_{yz}$) (*30, 135*). The UV-visible spectral data for *trans*-$[Ru^V(L)(O)_2]^+$ in acetonitrile are collected in Table III. The low-energy vibronic structured absorption band at 420–450 nm has been assigned as the ligand–field $d_{xy} \rightarrow d_\pi{}^*$ transition, which is red-shifted when compared with that of the parent *trans*-$[Ru^{VI}(L)(O)_2]^{2+}$ (*30*) (Table III) (see also Section II,C,1,c). The intense band at 290–295 nm is tentatively assigned as the lowest energy $p_\pi(O) \rightarrow d_\pi{}^*(Ru)$ LMCT transition (*30*). The complex *trans*-$[Ru^V(N_2O_2)(O)_2]ClO_4$ has also been isolated and is stable in aqueous solution with pH ≤ 7 (*136*).

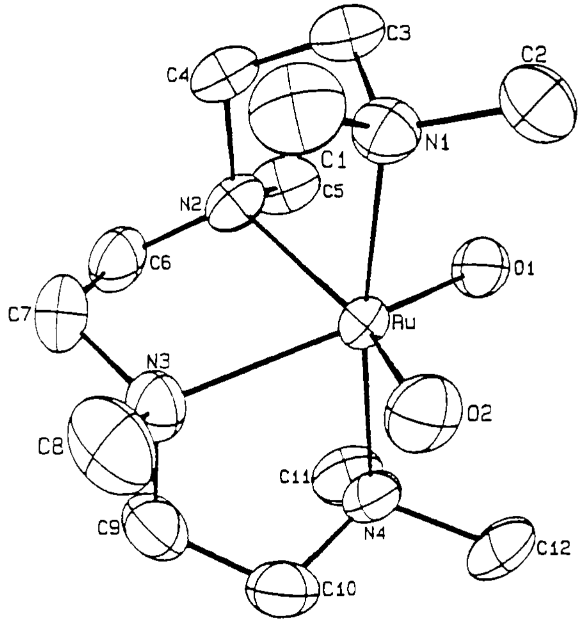


FIG. 7. ORTEP plot of *cis*-$[Ru^{V}(Tet\text{-}Me_6)(O)_2]^+$ cation with atomic numbering scheme. From Ref. *(134)*.

TABLE III

UV-VISIBLE SPECTRAL DATA OF *trans*-DIOXO(MACROCYCLIC TERTIARY AMINE) COMPLEXES OF Ru(VI), Ru(V), Os(VI), Os(V) IN ACETONITRILE

Complex	λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	
	$^1[(d_{xz},d_{yz}) \leftarrow (d_{xy})]$	$^3[(d_{xz},d_{yz}) \leftarrow (d_{xy})]$
trans-$[Ru^{VI}(14TMC)(O)_2]^{2+}$	388 (560)	455sh (50)
trans-$[Ru^{VI}(15TMC)(O)_2]^{2+}$	377 (550)	430sh (50)
trans-$[Ru^{VI}(16TMC)(O)_2]^{2+}$	375 (670)	425sh (80)
trans-$[Ru^{V}(14TMC)(O)_2]^{+}$	422 (240)	525sh (20)
trans-$[Ru^{V}(15TMC)(O)_2]^{+}$	420 (260)	530sh (20)
trans-$[Ru^{V}(16TMC)(O)_2]^{+}$	448 (170)	550sh (10)
trans-$[Os^{VI}(14TMC)(O)_2]^{2+}$	312 (1260)	355 (340)
trans-$[Os^{VI}(15TMC)(O)_2]^{2+}$	307 (1815)	347 (475)
trans-$[Os^{VI}(16TMC)(O)_2]^{2+}$	306 (1915)	346 (345)
trans-$[Os^{V}(14TMC)(O)_2]^{+}$	335 (490)	410 (100)
trans-$[Os^{V}(15TMC)(O)_2]^{+}$	332 (540)	410 (120)
trans-$[Os^{V}(16TMC)(O)_2]^{+}$	330 (550)	410 (160)

An analogous series of *trans*-$[Os^V(L)(O)_2]ClO_4$ complexes have also been isolated and characterized (L = 14TMC, 15TMC, 16TMC, $CRMe_3$) (*75, 137*). The *trans*-$[Os^V(14TMC)(O)_2]ClO_4$ complex was similarly prepared by constant potential reduction of *trans*-$[Os^{VI}(14TMC)(O)_2](ClO_4)_2$ in MeCN (0.1 *M* Bu_4NClO_4) at −0.75 V vs $Cp_2Fe^{+/0}$ couple (*137*). A μ_{eff} value of 1.89 μ_B has been obtained for *trans*-$[Os^V(14TMC)(O)_2]ClO_4$. The IR spectrum shows two intense absorption bands at 879 and 873 cm^{-1}, tentatively assigned as the $\nu_{asym}(Os{=}O)$ stretch. The observation of two bands has been suggested to arise as a result of solid-state splitting due to low site symmetry. The UV-visible spectral data for *trans*-$[Os^V(L)(O)_2]^+$ in acetonitrile are collected in Table III. The UV-visible absorption spectra exhibit two vibronic structured bands, centered at ~335 and 410 nm, assigned as the respective spin-allowed and -forbidden $d_{xy} \rightarrow d_\pi{}^*$ transitions. These bands are also red-shifted with respect to the parent Os(VI) complexes. Such red shifts have been attributed to the splitting of the doubly degenerate $d_\pi{}^*$ orbitals of d^3 osmium(VI) as well as the lowering of its energy level by occupancy of an electron in the antibonding $d_\pi{}^*$ orbitals. Similar red shifts have been reported for the isoelectronic ruthenium(VI) and -(V) systems (*30*).

The *trans*-$[Ru^V(L)(O)_2]^+$ complexes (*138*) are found to disproportionate in acidic solutions:

$$2\textit{trans}\text{-}[Ru^V(L)(O)_2]^+ + 2H^+ \rightarrow \textit{trans}\text{-}[Ru^{VI}(O)(O)_2]^{2+} + \textit{trans}\text{-}[Ru^{IV}(L)(O)(OH_2)]^{2+}$$

The disproportionation equilibrium constant, K_{disp}, and the $E_{1/2disp}$ for the reaction have been calculated to be 0.86 V and 3.18×10^{11} mol^{-1} dm^3 for *trans*-$[Ru^V(14TMC)(O)_2]^+$ at 25°C. A K_{disp} and $E_{1/2disp}$ of 2.77×10^7 mol^{-1} dm^3 and 0.44 V at pH 1.1 and 25°C have also been obtained for the *trans*-$[Ru^V(N_2O_2)(O)_2]^+$ system (*136*). The lower K_{disp} value compared to that of the 14TMC system has been attributed to the weaker donor strength of the N_2O_2 ligand, which would destabilize the Ru(VI) complex, leading to a higher Ru(VI/IV) redox potential.

The mechanism for the rapid disproportionation of *trans*-$[Ru^V(14TMC)(O)_2]^{2+}$ has been studied in detail (*138*). It has been found that the disproportionation reaction where L = 14TMC follows the rate law rate = $k_{disp}[Ru^V]^2$, with $k_{disp} = 2k_eK_p[H^+]/(1 + K_p[H^+])^2$, where K_p and k_e are the equilibrium constant and rate constant for the respective reactions

$$\textit{trans}\text{-}[Ru^V(14TMC)(O)_2]^+ + H^+ \rightarrow \textit{trans}\text{-}[Ru^V(14TMC)(O)(OH)]^{2+}$$

and

$$\textit{trans}\text{-}[Ru^V(14TMC)(O)(OH)]^{2+} + \textit{trans}\text{-}[Ru^V(14TMC)(O)_2]^+ \rightarrow$$
$$\textit{trans}\text{-}[Ru^{IV}(14TMC)(O)(OH)]^+ + \textit{trans}\text{-}[Ru^{VI}(14TMC)(O)_2]^{2+}$$

At 299 K and $I = 0.1$ mol dm^{-3}, K_p and k_e have been determined to be 615 ± 50 mol^{-1} dm^3 and $(2.72 \pm 0.34) \times 10^6$ mol^{-1} dm^3 s^{-1}, respectively (*138*). The self-exchange rate constant of the *trans*-[Ru^{V}(14TMC)(O)(OH)]$^{2+}$/*trans*- [Ru^{IV}(14TMC)(O)(OH)]$^+$ has been estimated to be 5×10^3 mol^{-1} dm^3 s^{-1} at 298 K and $I = 0.1$ mol dm^{-3} (*138*).

Addition of a small drop of CF_3COOH to an acetonitrile solution of *trans*-[Os^{V}(14TMC)(O)$_2$]$^+$ led to an immediate disappearance of Os(V) and concomitant formation of Os(VI) (*75, 137*):

$$3\textit{trans}\text{-}[\mathrm{Os^{V}(L)(O)_2}]^+ + 3\mathrm{H}^+ \rightarrow 2\textit{trans}\text{-}[\mathrm{Os^{VI}(L)(O)_2}]^{2+} + 2\textit{trans}\text{-}[\mathrm{Os^{III}(L)(OH)(OH_2)}]^{2+}$$

Unlike the *trans*-[Ru^{V}(L)(O)$_2$]$^+$ case where a simple disproportionation reaction to Ru(VI) and Ru(IV) occurs, the reaction has been complicated by the instability of the oxoosmium(IV) species, which is found to disproportionate to Os(V) and Os(III) even under alkaline conditions (*75, 137*).

Monooxo complexes of ruthenium(V), *trans*-[Ru^{V}(L)(O)(X)]$^{2+}$ (L = 14TMC; X = Cl$^-$, NCO$^-$, N$_3$$^-$), have been generated electrochemically from the parent Ru(IV) oxo complexes in acetonitrile (*31, 139*). These complexes have high one-electron reduction potentials with E^0[Ru(V)/Ru(IV)] ranging from 1.10 to 0.70 V vs Ag/AgNO$_3$ (0.1 mol dm^{-3} in MeCN). They have been demonstrated to be active toward the oxidation of benzyl alcohol to benzaldehyde. Second-order rate constants for the reaction between *trans*-[Ru^{V}(L)(O)(X)]$^{2+}$ and benzyl alcohol have been evaluated by rotating disk voltammetry. Values of 2.1×10^2 and 1.4×10^2 mol^{-1} dm^3 s^{-1} have been obtained for X = Cl$^-$ and NCO$^-$, respectively, assuming the following mechanism:

$$\mathrm{Ru^{IV}} - e^- \rightleftharpoons \mathrm{Ru^{V}}$$

$$\mathrm{Ru^{V}} + \mathrm{PhCH_2OH} \xrightarrow{k} \mathrm{Ru^{IV}} + \mathrm{Ph\dot{C}HOH} + \mathrm{H^+}$$

$$\mathrm{Ru^{V}} + \mathrm{Ph\dot{C}HOH} \xrightarrow{\text{fast}} \mathrm{Ru^{IV}} + \mathrm{PhCHO} + \mathrm{H^+}$$

In aqueous solution, *cis*-[Ru^{V}(pyen)(O)Cl]$^{2+}$ has also been generated electrochemically (*140*). This Ru(V) oxo complex has an E^0[Ru(V/IV)] value of 1.29 V vs SCE and oxidizes benzyl alcohol with a second-order rate constant of 8.4×10^4 dm^3 mol^{-1} s^{-1} at 25°C (*140*).

A monooxoruthenium(V) complex of a pentadentate N$_4$O$^-$ ligand, [Ru^{V}(N$_4$O)(O)](ClO$_4$)$_2$ [N$_4$OH = bis(2-(2-pyridyl)ethyl)(2-hydroxy-2-(2-pyridyl)ethyl)amine], has been obtained by Ce(IV) oxidation of [Ru^{III}(N$_4$O)(OH$_2$)](ClO$_4$)$_2$; the structure of the latter has been confirmed by X-ray crystallography (*45*). Magnetic susceptibility measurement of [Ru^{V}(N$_4$O)(O)](ClO$_4$)$_2$ gave a μ_{eff} of 2.2 μ_B. The IR spectrum of [Ru^{V}(N$_4$O)(O)](ClO$_4$)$_2$ revealed an intense Ru=O stretch at 872 cm^{-1}, higher than the values of 790–810 cm^{-1} found in monooxoruthenium(IV) complexes such as *trans*-$[Ru^{IV}(14TMC)(O)(X)]^{n+}$ (X = Cl, NCO, N_3, CH_3CN) (*30*) and $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ (*26*), suggesting a stronger Ru=O bond in Ru(V) than Ru(IV). Its electrochemistry in aqueous solution has been found to be associated with proton-coupled electron-transfer reactions. At pH 1, a two-electron two-proton $[Ru^{V}(N_4O)(O)]^{2+}/[Ru^{III}(N_4O)(OH_2)]^{2+}$ couple at 1.02 V vs SCE is observed:

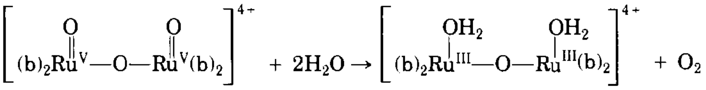
$$[Ru^{V}(N_4O)(O)]^{2+} + 2H^{+} + 2e^{-} \rightarrow [Ru^{III}(N_4O)(OH_2)]^{2+}$$

At 5.5 > pH > 3.5, the wave for the Ru(V/III) couple splits into two waves, a pH-independent one-electron wave for the $[Ru^{V}(N_4O)(O)]^{2+}/[Ru^{IV}(N_4O)(O)]^{+}$ couple (slope = 0 mV/pH unit) and a two-proton one-electron $[Ru^{IV}(N_4O)(O)]^{+}/[Ru^{III}(N_4O)(OH_2)]^{2+}$ couple (*45, 141*).

The $[Ru^{V}(N_4O)(O)]^{2+}$ complex is shown to oxidize a variety of organic substrates such as alcohols, alkenes, THF, and saturated hydrocarbons, which follows a second-order kinetics with rate = k[Ru(V)][substrate] (*142*). The oxidation reaction is accompanied by a concomitant reduction of $[Ru^{V}(N_4O)(O)]^{2+}$ to $[Ru^{III}(N_4O)(OH_2)]^{2+}$. The mechanism of C—H bond oxidation by this Ru(V) complex has also been investigated. The C—H bond kinetic isotope effects for the oxidation of cyclohexane, tetrahydrofuran, propan-2-ol, and benzyl alcohol are 5.3 ± 0.6, 6.0 ± 0.7, 5.3 ± 0.5, and 5.9 ± 0.5, respectively. A mechanism involving a linear [Ru=O···H···R] transition state has been suggested for the oxidation of C—H bonds. Since a linear free-energy relationship between log(rate constant) and the ionization potential of alcohols is observed, facilitation by charge transfer from the C—H bond to the Ru=O moiety is suggested for the oxidation.

Monooxoruthenium(V) complexes of Schiff base ligand $[Ru(O)(saloph)X]^{n+}$ [saloph = *N,N'*-bis(salicylidene)-*o*-phenylene-diaminato-; X = Cl, imidazole, or 2-Me-Im] (*143*) and [Ru(edta)(O)] (*144*) have also been claimed by Khan and co-workers, but further characterization of these species is required.

Oxo-bridged ruthenium(V)–(V) dimers of polypyridyl ligands have been suggested as intermediates for the oxidation of H_2O to O_2 in a concerted four-electron step (*62, 63*):



$$\left[(b)_2\overset{\overset{\displaystyle O}{\|}}{Ru^{V}}—O—\overset{\overset{\displaystyle O}{\|}}{Ru^{V}}(b)_2\right]^{4+} + 2H_2O \rightarrow \left[(b)_2\overset{\overset{\displaystyle OH_2}{|}}{Ru^{III}}—O—\overset{\overset{\displaystyle OH_2}{|}}{Ru^{III}}(b)_2\right]^{4+} + O_2$$

(b = substituted 2,2′-bipyridine, or 1,10-phenanthroline).

The best catalyst for water oxidation so far is with b = 5,5′-$(COOH)_2$-bpy reported by Grätzel and co-workers (*145*).

These μ-oxo-bridged Ru(V)═O complexes were generated by electrochemical or chemical oxidations of the corresponding ruthenium(III) aqua precursors in aqueous solutions and are very reactive with high E^0 values. The rate of oxidation of water to oxygen by $[(bpy)_2(O)Ru^{V}ORu^{V}(O)(bpy)_2]^{4+}$ has been estimated to be a first-order process with rate = k_{obs}[Ru(V)—Ru(V)], where k_{obs} is 0.01 s^{-1} at 298 K (μ = 0.1 *M*) (*63*).

Other dinuclear Ru(V)═O complexes such as $[(bpy)_2(O)Ru^{IV}ORu^{V}(O)(bpy)_2]^{3+}$ (*63*) and $[(bpy)_2(py)Ru^{III}O—Ru^{V}(O)(bpy)_2]^{4+}$ (*146*) have been isolated and are facile oxidants toward a variety of organic functional groups. The rate constants for the oxidation of propan-2-ol are 2.5 and 6.9 M^{-1} s^{-1}, respectively (*63, 146*), which are substantially higher than the corresponding value of 8.7×10^{-3} M^{-1} s^{-1} found for $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ (*51*). The complex $[(bpy)_2(O)Ru^{IV}ORu^{V}(O)(bpy)_2]^{3+}$ could also oxidize H_2O to O_2 by a pH-independent reaction that is first order in oxidant [k(298 *K*, μ = 0.1 *M*) = 3.0×10^{-4} s^{-1}] (*63*).

The osmium complex $[(bpy)_2(O)Os^{V}—O—Os^{V}(O)(bpy)_2]^{4+}$ has also been generated in a manner similar to that of its ruthenium analog (*76*). Electrochemically, the redox couples $Os^{II}—Os^{II}$, $Os^{III}—Os^{III}$, $Os^{III}—Os^{IV}$, $Os^{IV}—Os^{IV}$, $Os^{IV}—Os^{V}$, and $Os^{V}—Os^{V}$ are all accessible. The Pourbaix diagrams for $[(bpy)_2(H_2O)Os^{III}—O—Os^{IV}(OH)(bpy)_2]^{4+}$ and $[(bpy)_2(H_2O)Ru^{III}—O—Ru^{III}(OH_2)(bpy)_2]^{4+}$ have been studied and are shown in Figs. 8 and 9.

d. Group VI Ligands. Reaction of $[Pr_4{}^nN][RuO_4]$ in acetone with 2-hydroxy-2-ethylbutyric acid in a 1 : 2 mole ratio over 48 h at 25°C gives a red-brown solution from which brown crystals of $[Pr_4{}^nN][Ru(O)(O_2COCEt_2)_2]$ have been isolated by addition of *n*-hexane, which has been established by X-ray crystallography (Fig. 10) (*147*). Two crystallographically independent molecules have been obtained with Ru═O distances of 1.697(5) and 1.676(6) Å. Magnetic susceptibility measurements showed that $[Ru(O)(O_2COCEt_2)_2]^-$ is paramagnetic. Electron spin resonance (ESR) studies in a CH_2Cl_2—MeOH glass at ~100 K suggest that the complex has a single unpaired electron in the ground state, consistent with a penta-coordinate Ru(V) configuration (*147, 148*). The complex $[Ru(O)(O_2COCEt_2)_2]^-$ has been found to function as a mild oxidant in MeCN, capable of slowly oxidizing alcohols to aldehydes or ketones and PPh_3 to $OPPh_3$. Catalytic oxidation reactions employing *N*-methyl-morpholine *N*-oxide (NMO) as cooxidant have also been investigated (*147*).

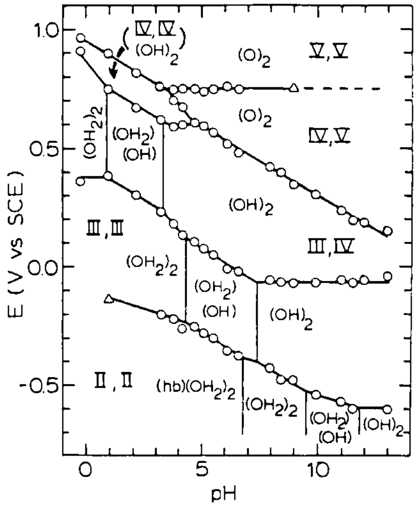


FIG. 8. Pourbaix diagram for $[(bpy)_2(OH_2)Os^{III}OOs^{IV}(OH)(bpy)_2]^{4+}$. From Ref. (*76*).

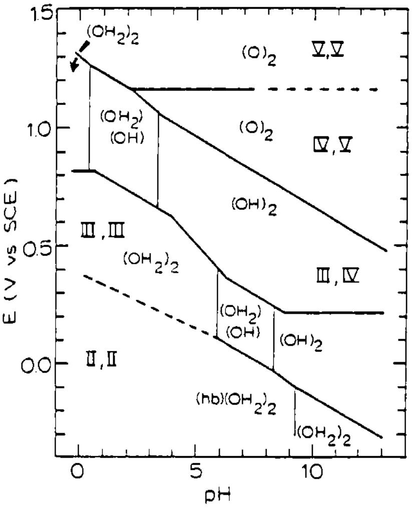


FIG. 9. Pourbaix diagram for $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$. From Ref. (*62*).

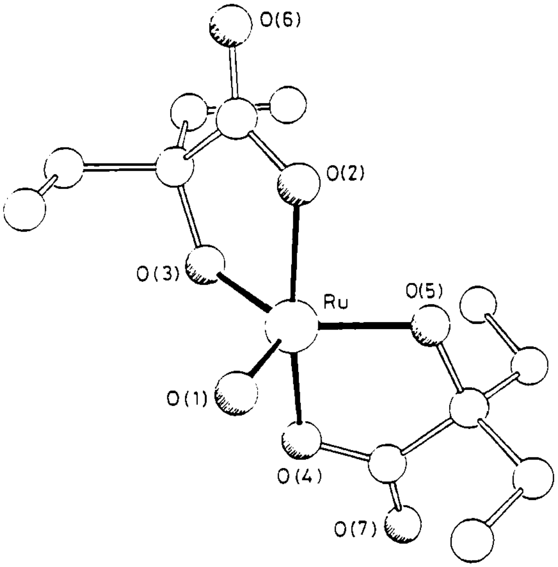


FIG. 10. Perspective view of the structure of the $[Ru(O)(O_2COCEt_2)_2]^-$ anion. From Ref. (*147*).

Similarly, a series of oxoruthenium(V) complexes with α-hydroxy carboxylate $[Pr_4{}^nN][Ru(O)(O_2COCR^1R^2)_2]$ (R^1R^2 = Me_2, EtMe, PhMe) and α-amino carboxylate ligands $[Pr_4{}^nN][Ru(O)(O_2C(NH)CHEt)_2]$ have been prepared by Dengel and Griffith by the reaction of $[Pr_4{}^nN][RuO_4]$ with the appropriate acid in acetone. The osmium analog, for which only $[Ph_4P][Os(O)(O_2COCEt_2)_2]$ is isolated in a pure state, was similarly prepared from $[Ph_4P][OsO_4]$ and 2-hydroxy-2-ethylbutyric acid in acetone and characterized by IR spectroscopy with a ν(Os=O) stretch at 958 cm^{-1} (*148*).

Bercaw and co-workers reported the formation of a binuclear Ru(V)=O complex, $[L_{OEt}(O)Ru(\mu\text{-}O)_2Ru(O)L_{OEt}]$, where L_{OEt} = $[CpCo\{(EtO)_2P{=}O\}_3]^-$ (*149*). This complex, although diamagnetic, has Ru—Ru separation of 2.912 Å. It consists of two Ru=O moieties bridged by two oxo ligands. The Ru=O and Ru—O(bridging) distances are 1.725(3) and 1.887(4) Å, respectively.

2. *Nitrido Complexes*

An osmium(V) nitrido complex $[Os(N)(CO)(NH_3)_4]^{2+}$ has been suggested to be involved in the formation of $[Os_2(N_2)(NH_3)_8(CO)_2]^{4+}$ by oxidation of $[Os(NH_3)_5(CO)]^{2+}$ (*150*). An osmium(IV)–(V) species,

$[Os_2N(S_2CNR_2)_5]^+$, has been observed as an intermediate in the reversible one-electron oxidation of $Os_2N(S_2CNR_2)_5$ (R = Me, Et) and possibly, an osmium(V) dimer is formed on further irreversible oxidation (*84*). The complex $[Os^V(NH_3)_4(N)]^{2+}$ has been generated by reductive quenching of the ^3E_g state of $[Os^{VI}(NH_3)_4(N)]^{3+}$ (*151*). This species, once formed, undergoes rapid coupling with $[Os^{VI}(NH_3)_4(N)]^{3+}$ to form the novel mixed-valence $[Os_2(NH_3)_8(CH_3CN)_2(\mu\text{-}N_2)]^{5+}$ (*151*) (see Section II,C,2).

3. *Imido Complexes*

No imido complex of osmium(V) has yet been isolated. Wilkinson and co-workers reported that reactions of $Ru_2(O)_2(CH_2SiMe_3)_6$ with PhNCO and $Me_3P{=}NSiMe_3$ gave $Ru_2(NPh)_2(CH_2SiMe_3)_6$ and $Ru_2(NSiMe_3)_2(CH_2SiMe_3)_6$, respectively (*130*). These Ru(V) imido complexes, which were characterized by ^1H NMR spectroscopy, are very unstable and oxygen sensitive. The Ru=NPh and $Ru{=}NSiMe_3$ stretches were found at 1132 and 1160 cm^{-1}, respectively (*130*).

4. *Other Complexes*

Osmium(V) porphyrin complexes, $[Os^V(P)(OR)_2]^+$, have recently been generated by electrochemical oxidation of the corresponding $[Os^{IV}(P)(OR)_2]$ and were characterized by UV–VIS spectroscopy (*112*). The $[Os^V(salen)(OR)_2]^+$ complexes have been generated and characterized in a similar manner (*152*).

C. OXIDATION STATE +VI

1. *Oxo Complexes*

Monooxo and *cis*- and *trans*-dioxo complexes of ruthenium(VI) and osmium(VI) are known, with the *trans*-dioxo species being most common (*1*). In general, these complexes are all diamagnetic and are characterized by vibrational spectroscopy and/or X-ray crystallography. One intense metal–oxo stretch is usually observed for monooxo and *trans*-dioxo complexes while two metal–oxo stretches, $\nu_s(MO_2)$ and $\nu_{as}(MO_2)$, are found for the *cis*-dioxo species in the IR spectra. The structural and vibrational data are listed in Table I.

a. Oxides and Oxoanions. Ruthenate(VI) ions are known. The single-crystal X-ray structure of "$BaRuO_4 \cdot H_2O$" has been obtained and was shown to have the molecular structure $Ba[RuO_3(OH)_2]$ with a trigonal bipyramidal anion with *trans* axial OH groups [d(Ru—OH) = 2.02 Å, d(Ru=O) = 1.755 Å] (*153*). However, in solution, the $[RuO_4]^{2-}$

ion has been suggested to be the major species present and its vibrational data have been measured (*154, 155*). Both the Mössbauer spectrum (*156*) and electrochemistry of $[RuO_4]^{2-}$ (*157*) have been reported, respectively. The oxidation of organic substrates, both stoichiometric and catalytic, by $[RuO_4]^{2-}$ and $Ba[Ru(OH)_2O_3]$ have been studied (*158–160*). The reagents are less reactive toward carbon–carbon double bonds than RuO_4, $[RuO_4]^-$, or OsO_4 and have been employed for the oxidation of a wide range of alcohols to aldehydes and ketones without attack of double bonds (*159, 160*). The kinetics and mechanism of the oxidation of alcohols and substituted mandelic acids by ruthenate ions have been investigated in detail (*161*). A concave upward Hammett plot was obtained for the oxidation of substituted mandelic acids (*161*). The involvement of free radical-like transition states resulting from the decomposition of organometallic intermediates has been suggested to account for the concave upward Hammett plot by Lee and Congson (*161*).

A substantial number of hexa-, penta-, and tetraoxo species of Os(VI) have been reported, such as $[OsO_6]^{6-}$, $[OsO_5]^{4-}$, and $[OsO_4]^{2-}$ ions. However, it is uncertain whether they contain discrete mononuclear species or not. Examples reported include $Li_6[OsO_6]$, $Na_4[OsO_5]$, $Ba_2[OsO_5]$, and $Ba_3[OsO_6]$ (*162*). Mixed oxides with ordered perovskite structures $A_2B[OsO_6]$ (A = Sr, Ca, Ba; B = Mg, Zn, Al, etc.) are known (*163*).

Oxohalides of the form $RuOF_4$, $OsOF_4$, and $OsOCl_4$ have been reported. The best preparations of $OsOF_4$ are from OsO_4/OsF_6 in a 1:3 ratio at 175°C (*164*) or from OsF_6 and B_2O_3 (*165*). The Raman spectrum of the solid shows an Os═O stretch at 1009 cm^{-1} (*166*). A clear-cut method to prepare $RuOF_4$ from RuO_4 and KrF_2 has been reported (*167*). Its IR spectrum shows a strong ν(Ru═O) stretch at 900 cm^{-1} (*167*). The diamagnetic $M_2[Ru(O)_2Cl_4]$ (M = Cs, Rb) can be prepared by treating RuO_4 with an excess of MCl in dilute HCl (*87*). The complex $Cs_2[Ru(O)_2Br_4]$ has been similarly prepared from RuO_4 and CsBr/HBr and characterized by IR spectroscopy with a $\nu_{as}[Ru(O)_2]$ stretch at 825 cm^{-1} (*87*). The octahedral structure of $[Ru(O)_2Cl_4]^{2-}$ of the $(Ph_3P)_2N^+$ salt has been established by X-ray crystallography to consist of *trans*-dioxo ligands with d(Ru═O) = 1.709(4) Å and by IR spectroscopy (*168*) (Table I). The trigonal–bipyramidal structure of $[Ru(O)_2Cl_3]^-[(Ph_3P)_2N]^+$ with the *cis*-dioxo ligands has also been established by X-ray crystallography with d(Ru═O) of 1.658(5) and 1.694(9) Å and O—Ru—O angle of 127° (*168*). Oxygen atom transfer reactions from $[Ru(O)_2Cl_3]^-$ to phosphines, alkenes, and phenols have been studied (*168*). The complex $[Ru(O)_2Cl_3](Ph_4P)$ has also been shown to be a mild and selective two-electron oxidant for alcohols (*160*). Salts of the form *trans*-$[R\text{-}pyH]_2[Ru(O)_2Cl_4]$ (R-py = pyridine, substituted pyridines), *trans*-$R_2[Ru(O)_2X_4]$ [X = Cl, Br; R = $Me_2NH(CH_2)_2NHMe_2$, $Me_2N(C_2H_4)_2NMe_2$], $(Ph_4P)[Ru(O)_2Br_3]$, *trans*-$(Ph_4P)_2[Ru(O)_2Br_4]$, and *trans*-$(Ph_4As)[Ru(O)_2Cl_3(OPPh_3)]$ have been shown to function as two-electron catalysts for the oxidation of primary alcohols to aldehydes and of secondary alcohols to ketones, without competing olefinic bond cleavage, in the presence of NMO as cooxidant (*169*).

An X-ray study has also been reported for the osmium analog $K_2[Os(O)_2Cl_4]$ made from $K_2[Os(O)_2(OH)_4]$ and Cl^-, or OsO_4 and HCl. A *trans*-OsO_2 geometry is observed with $d(Os{=}O) = 1.750(22)$ and $d(Os{-}Cl) = 2.379(5)$ Å (*170*).

b. Group IV Ligands. The cyano complex $K_2[Os(O)_2(CN)_4]$ is made from the action of aqueous KCN solution on OsO_4. The X-ray crystal structure of $Cs_2[Os(O)_2(CN)_4]$ has been determined with Os=O distance = 1.750(8) Å (*171*). Attempts to prepare the ruthenium analog using RuO_4 and NaCN gave the paramagnetic green complex $Cs_3[Ru(O)(CN)_4(NCO)_2]$ (*87*) (see Section II,B,1,b). The photochemistry of $[Os(O)_2(CN)_4](Ph_4As)_2$ has been reported (*172–174*). The complex has been shown to exhibit photoluminescence at ~710 nm with an excited-state lifetime of 0.4 μs in degassed acetonitrile (see Section II,C,1,c). Irradiation of $[Os(O)_2(CN)_4](Ph_4As)_2$ with light ($\lambda > 330$ nm) in the presence of organic substrates yields the corresponding oxidized organic products and $[Os^{II}(MeCN)_2(CN)_4](Ph_4As)_2$ (*174, 175*). Photo-induced oxygen atom transfer reactions have been observed with trialkylphosphines, dialkyl sulfides, and alkenes (*175*).

The interaction of OsO_4 with mesitylmagnesium bromide in THF and subsequent oxidation leads to the isolation of the green diamagnetic $Os(O)_2(mes)_2$, which is air stable both in solid form and in solutions (*176*). The X-ray crystal structure of $Os(O)_2(mes)_2$ has been determined to reveal tetrahedral geometry (Fig. 11). The $d(Os{=}O)$ bond distances are found to be 1.690(7) and 1.700(7) Å, with an O—Os—O bond angle of 136.1(3)° (*176*). A comparison between the structure of $Os(O)_2(mes)_2$ and that of $Re(O)_2(mes)_2$ has been made. The difference in structure has been suggested to result from the greater deforming effect of a filled nonbonding orbital in the diamagnetic d^2 Os^{VI} complex when compared with a half-filled orbital in the d^1 Re^{VI} analog (*176*). The IR spectrum of $Os(O)_2(mes)_2$ shows two strong peaks at 950 and 918 cm^{-1} and are assigned to the $\nu(Os{=}O)$ stretches of the *cis*-OsO_2 unit.

Reaction of $(Me_3SiCH_2)_2Mg$ with OsO_4 or $(Ph_4P)_2[Os(O)_2Cl_4]$ at $-70°C$ yields a dark brown-yellow diamagnetic crystalline solid,

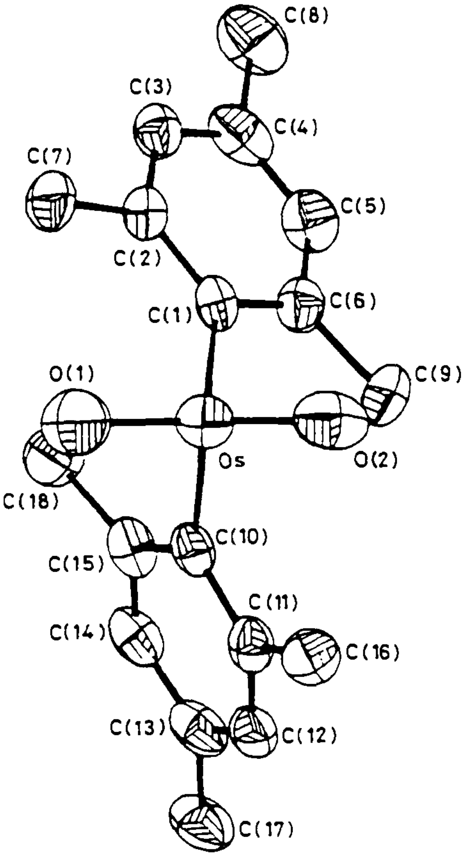


FIG. 11. Molecular structure of $Os(mes)_2(O)_2$. From Ref. (*176*).

$(Me_3SiCH_2)_4Os(O)$, which is monomeric (*177*). Its X-ray crystal structure has been determined: $d(Os{=}O) = 1.692(6)$ Å. The geometry about the osmium is distorted square pyramidal, with the four α-carbon atoms forming the base of the pyramid and the osmium atom slightly above the plane of the base. A similar reaction between $(Me_3SiCH_2)MgCl$ and $[PPN]_2[Ru(O)_2Cl_4]$ produced $(Me_3SiCH_2)_4Ru(O)$ (*178*). Unlike the osmium analog, $(Me_3SiCH_2)_4Ru(O)$ is sensitive to air and water. Interestingly, both Os(VI) and Ru(VI) complexes exhibit a reversible oxidation couple at similar potentials, 1.19 vs 1.20 V vs Ag/AgCl in CH_2Cl_2 (*178*). An Os=O stretch of 1054 cm^{-1} for $(Me_3SiCH_2)_4Os(O)$ has been reported by Shapley and co-workers (*178*), which is different from that of 1040 cm^{-1} reported by Wilkinson and co-workers (*177*).

Reaction of $(Me_3SiCH_2)_4Os(O)$ with carbon monoxide under conditions of elevated pressure and temperature gave $Os(CO)_5$, CO_2, and $(Me_3SiCH_2)_2CO$. The complex is found to be remarkably stable toward electrophilic attack, being stable even in 12 *N* aqueous HCl (*6*).

Interaction of $Os(O)_2(mes)_2$ with pyridines, isocyanides, and tertiary phosphines gave rise to complexes such as *trans*-$[Os(O)_2(bpy)(mes)_2]$, $[Os(O)_2(2{,}6\text{-}Me_2C_6H_3NC)(mes)_2]$, and $[Os(O)_2(PMePh_2)_2(mes)_2]$ (*179*). An oxoimido complex, $[Os(O)(NBu^t)(mes)_2]$, has also been synthesized and characterized by X-ray crystallography (*179*). The metal coordination is distorted tetrahedral with $d(Os{=}O) = 1.739(12)$ Å and $d(Os{=}N) = 1.731(12)$ Å. The Os—N—C(Bu^t) angle is 161(1)°, indicating a linear four-electron mode of bonding analogous to an oxo function. The Os—N distance is marginally shorter than the Os—O distance despite the reverse relationship for covalent radii, supporting evidence that the imido ligand is a better π-donor ligand than oxo. The O—Os—NR angle is only 121.5(6)°, much smaller than the O—Os—O angle in $Os(O)_2(mes)_2$. This, together with the slightly increased Os—C(mes) distances [2.12 and 2.16(1) compared with 2.05(1) Å in $Os(O)_2(mes)_2$], has been suggested to result from the increased steric compression in the molecule arising out of the additional presence of the *tert*-butyl group.

Herrmann and co-workers synthesized $[Os(O)(Me)_4]$ from OsO_4 and dimethylzinc or methyltris(isopropoxy)titanium (*180*). An alternative route is by methylation of the glycolate osmium(VI) complex $[O{=}Os(OCH_2CH_2O)_2]$ with dimethylzinc (*180*). The thermally labile ethyl derivative $[Os(O)(Et)_4]$ has also been prepared (*180*). $[Os(O)(Me)_4]$ is an orange, air-stable, volatile, crystalline compound that melts at 74°C without decomposition. The gas-phase average molecular structure of $[Os(O)(Me)_4]$, determined by electron diffraction techniques, is consistent with a theoretical model of C_4 symmetry with $d(Os{-}C) = 2.096(3)$ Å, $d(Os{=}O) = 1.681(4)$ Å, and $\angle O{-}Os{-}C = 112.2(5)°$ (*180*). Cyclic voltammetric studies showed that $[Os(O)(Me)_4]$ undergoes reversible reduction at -1.58 V and an irreversible oxidation at $+2.2$ V vs Ag/AgCl in MeCN.

Other organoosmium oxo complexes include *cis*-$[(Me_3SiCH_2)_2(Me)_2Os(O)]$, $Os(O)_2Me_2(py)_2$, $(Me_3SiCH_2)_2Os(O)_2(py)_2$, $[(Me)_2Os(O)_2(py)]_3$, and $(Me)_2(O)Os[OC(Me)_2C(Me)_2O]$. The complex $Os(O)_2(Me)_2(py)_2$ has been obtained by the exchange of a glycolate chelating ligand on $Os(O)_2(py)_2(gly)$ for two methyl groups (*181*). Similarly, the $Os(O)_2(py)_2(CH_2SiMe_3)_2$ complex is prepared from $Os(O)_2(py)_2(gly)$ and bis(trimethylsilylmethyl)zinc. The structures of both $\mathrm{Os(O)_2(Me)_2(py)_2}$ and $\mathrm{Os(O)_2(py)_2(CH_2SiMe_3)_2}$ have been determined by X-ray crystallography [$\mathrm{Os(O)_2(Me)_2(py)_2}$, $d(\mathrm{Os{=}O}) = 1.723(3), 1.715(3)$ Å] (*181*).

In vacuum, $\mathrm{Os(O)_2(Me)_2(py)_2}$ loses one molar equivalent of pyridine to give the formally fivefold coordinated complex $\mathrm{Os(O)_2(Me)_2(py)}$ (*181*). In the solid state, the latter complex forms the trinuclear compound $[\mathrm{Os_3O_6(py)_3(Me)_6}]$, which is octahedrally coordinated at osmium (Fig. 12). The crystal structure is unusual in that an unsymmetrical, nearly planar $\mathrm{Os_3O_3}$ six-membered ring, held together by O → Os donor bonds, is present. However, these bonds stabilize only the solid-state structure and are so weak that only monomers exist even in chloroform or benzene. The $\mathrm{(Me)_2(O)O}\overline{\mathrm{s[OC(Me)_2C(Me)_2O}}\mathrm{]}$ complex is prepared by the reaction of the bulky bispinacolate complex with dimethylzinc (*181*). Removal of the second chelating ligand by Grignard reagents such as $\mathrm{Me_3SiCH_2MgCl}$ gives $\mathrm{Os(O)_2(Me)_2(CH_2SiMe_3)_2}$ (*181*).

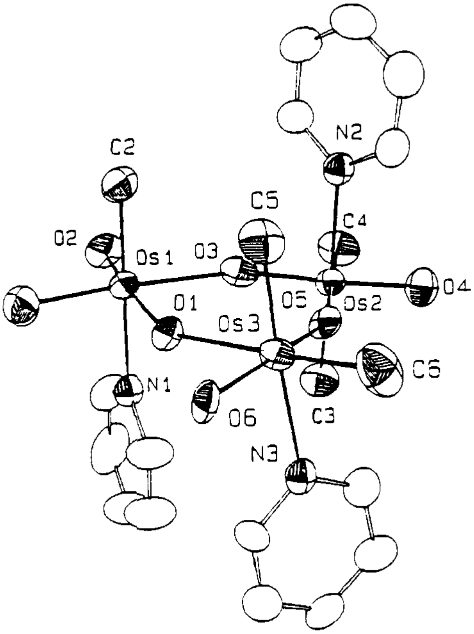


FIG. 12. Structure of trimeric dimethyl(dioxo)(pyridine)osmium(VI), $\mathrm{Os_3O_6(py)_3(Me)_6}$. From Ref. (*181*).

c. Group V ligands. The dark green solid produced by the action of RuO_4 in carbon tetrachloride on pyridine, originally formulated as $RuO_4 \cdot py_2$, is in fact *trans*-$[Ru^{VI}(py)_2(OH)_2(O)_2]$, which is diamagnetic with an IR absorption band at 790 cm^{-1}, assignable to the $\nu_{as}(RuO_2)$ stretch (*182*). A similar species formulated as RuO_4, $bpy \cdot 3H_2O$ has also been suggested by Griffith and Rossetti to contain a *trans*-RuO_2 unit, $[Ru^{VI}(bpy)(OH)_2(O)_2]$ (*182*).

More recently, "RuO_4,py_2" was further reformulated as a ruthenium(VI) dimer, $[Ru_2O_6(py)_4]$, on the basis of vibrational spectra, which was later confirmed by X-ray crystallography (Fig. 13) (*183*). The X-ray crystal structure of $[Ru_2O_6(py)_4] \cdot 3 \cdot 5H_2O$ shows a planar Ru_2O_2 bridge [d(Ru—O) = 1.93(1) Å] in which the Ru—O—Ru angle is 100.0(5)° with a terminal Ru=O bond length of 1.72(1) Å. It is distinctly nonlinear, with an O=Ru=O angle of 160.5(4)°. The reformulation of $[RuO_4(bpy)]$ as $[Ru_2O_6(bpy)_2]$ has also been suggested (*183*). Other complexes of the form $[Ru_2O_6L_4]$ [L = 4-*tert*-butylpyridine, nicotinic acid, isonicotinamide, pyridine-2-carboxylic acid, $\frac{1}{2}$(bpy)] have also been prepared (*183*). These dimeric complexes have been shown to function as overall eight-electron oxidants, converting primary alcohols into aldehydes and secondary alcohols into ketones, and function catalytically with *N*-methylmorpholine *N*-oxide or PhIO as cooxidant. The $[Ru_2O_6(py)_4]$ and $[Ru_2O_6(4\text{-}Bu^t\text{-}py)_4]$ complexes have been shown to effect oxidation of alcohols with dioxygen as cooxidant (*183*).

A similar compound, $[Os_2O_6(py)_4]$, prepared by the reaction of OsO_4 with pyridine in the presence of ethanol, originally formulated as $OsO_3(py)_2$ has been confirmed to be a dimer by single-crystal X-ray studies (*184*). The osmium is octahedral with *trans* osmyl linkages

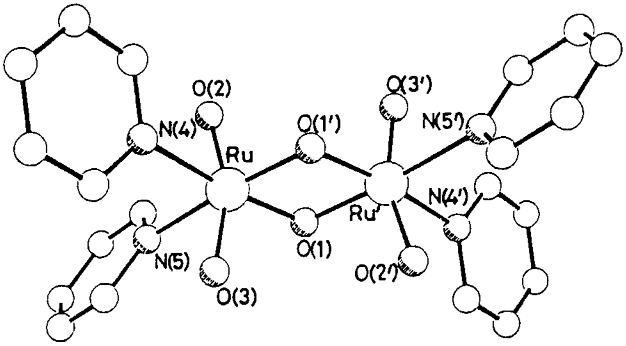


FIG. 13. Perspective view of the structure of $[Ru_2O_6(py)_4]$ with atom labeling. From Ref. (*183*).

[d(Os=O) = 1.73 Å], the osmyl O—Os—O angle being bent away from the Os_2O_2 bridge at 163.5(8)° with d(Os—N(py)) of 2.20(2) Å and a mean d(Os—O(bridge)) distance of 1.94 Å.

There is evidence that, in solution, the dimer is in equilibrium with monomer and there may be such equilibria between monomeric and dimeric forms with $Os_2O_6L_4$ [L = 3-picoline, 3-chloropyridine, ½(2,2′-bpy), imidazole, ½(1,10-phen), and TMEA] (*185*):

$$Os_2O_6L_4 \rightleftharpoons 2\ OsO_3L_2$$

Another Os(VI) dimer of similar structure is the $K_4[Os_2O_6(NO_2)_4]\cdot 6H_2O$, a deep brown crystalline material obtained by prolonged reaction of KNO_2 with OsO_4 in aqueous solution at room temperature. It was long formulated as "$K_2[OsO_3(NO_2)_2]\cdot 3H_2O$." A single-crystal X-ray study showed that it is a dimer with the osmyl Os=O distance 1.79(1) Å and the osmyl O—Os—O angle 164.1°, bent away from the Os_2O_2 bridge; the Os—N distance is 2.17(2) Å and the Os—O(bridge) distance is 1.99 Å with an Os—O—Os bridge angle of 102° (*186*).

Reaction of RuO_4 in CCl_4 with ice-cold mildly alkaline solutions of RCl (R = NH_4, Hbpy, or Hpy) yielded the species $[Ru^{VI}(NH_3)_4(O)_2]Cl_2$ (*87*), $[Ru^{VI}(bpy)(O)_2Cl_2]$ (*187*), and $[Ru^{VI}(py)_2(O)_2Cl_2]$ (*187*), all of which have been characterized by IR spectroscopy with $\nu_{as}[Ru(O)_2]$ at ~837–840 cm^{-1}.

A number of pyridine complexes of the form *trans*-$[Ru^{VI}(R\text{-}py)_4(O)_2]^{2+}$, *trans*-$[Ru^{VI}(R\text{-}py)_2(O)_2Cl_2]$, and *trans*-$[Ru^{VI}(R\text{-}py)(O)_2Cl_3]^-$ (R-py = py, 4-Bu^{t}py, 2- and 3-COOH-py, lutidines, picolines, and isonicotinamide) have been prepared (*187*). Cyclic voltammetry of the complexes gave rather ill-defined reduction waves; only in the case of *trans*-$[Ru^{VI}(py)_2(O)_2Cl_2]$ in dimethyl sulfoxide were well-defined waves observed with a reversible Ru^{VI}/Ru^{V}couple at E^0 = 0.66V vs Ag/AgCl (*187*). They are efficient overall four-electron oxidants of primary and secondary alcohols, with Ru^{VI} being reduced to Ru^{II} pyridine complexes. Catalytic oxidations with NMO as cooxidant and a limited degree of aerobic catalysis have also been reported (*187*).

Oxidation of $[Ru^{II}(trpy)(C_2O_4)(H_2O)]$ by Ce(IV) in 2 *M* $HClO_4$ was found to give *trans*-$[Ru^{VI}(trpy)(O)_2(H_2O)]^{2+}$, whose structure has been characterized by X-ray crystallography (*188*). The two oxo groups are *trans* to each other with an average Ru=O distance of 1.661 Å and an O=Ru=O angle of 171.3°. This species functions as a *cis*-directed four-electron oxidant in the oxidation of diphosphines.

The osmium complexes *trans*-$[Os^{VI}(py)_3(O)_2(H_2O)]^{2+}$ and *trans*-$[Os^{VI}(py)_2(O)_2X_2]$ (X = Cl, Br) have been prepared by Griffith and Rossetti by the treatment of potassium osmate with pyridine followed by addition of HBF_4 and HX, respectively (*187*). These complexes were characterized by IR and Raman (symmetric MO_2 stretch at ~900 cm^{-1}) spectroscopy. The electronic absorption spectra show bands at ~367 nm and 310–320 nm, characteristic of the *trans*-dioxoosmium(VI) moiety. A large number of *trans*-$[Os^{VI}(py)_2(O_2R)(O)_2]$ and *trans*-$[Os^{VI}(bpy)(O_2R)(O)_2]$ oxo ester complexes have also been prepared (*185*), which will be described in Section II,C,1,d.

The complexes prepared by the reaction of NH_3 and Me_3N with potassium ruthenate(VI), formulated as $[Ru^{VI}(NH_3)_2(OH)_2(O)_2]$ and $[Ru^{VI}(NMe_3)_2(OH)_2(O)_2]$, respectively, and the subsequent reaction of the former with hydrochloric acid to give a complex formulated as $[Ru^{VI}(NH_3)_2(H_2O)_2(O)_2]Cl_2$, have been reinvestigated (*83*). The $[Ru^{VI}(NH_3)_2(H_2O)_2(O)_2]Cl_2$ complex has been reformulated as a μ-nitrido-ruthenium(IV) complex, $(NH_4)_3[Ru_2NCl_8(H_2O)_2]$, and $[Ru^{VI}(NH_3)_2(OH)_2(O)_2]$ as $Ru_2N(OH)_5 \cdot nH_2O$ (*83*). An alternative reformulation of $[Ru^{VI}(NH_3)_2(OH)_2(O)_2]$ as the oxo-bridged dimer $[Ru_2O_6(NH_3)_4]$ has also been proposed (*189*).

A series of *trans*-$[Ru^{VI}(py)_2(O_2CR)_2(O)_2]$ complexes [R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, and C_6H_5] has been prepared from *trans*-$Ba[RuO_3(OH)_2]$, carboxylic acid, and pyridine in acetonitrile at 0°C (*190, 191*). The X-ray crystal structure of $[Ru^{VI}(py)_2(OAc)_2(O)_2]$ has been determined with a d(Ru=O) of 1.726(1) Å (*190*). The oxidative reactivity of these dioxoruthenium(VI) complexes has been discussed, especially with regard to the competitive insertion into C=C and saturated C—H bonds of olefins (*191*). A common pathway that involves an initial hydrogen atom transfer has been suggested to accommodate the uniform oxidation of diverse substrates of different polar properties such as alkane, arene, alkene, and ether.

Complexes of *trans*-$[Ru^{VI}(b)_2(O)_2]^{2+}$ [b = 5,5′-Me_2bpy (*192*), bpy (*193*), phen (*194*)] and *cis*-$[Ru^{VI}(b')_2(O)_2]^{2+}$ [b′ = 6,6′-Cl_2bpy (*195*), 2,9-Me_2phen (*196*)] have also been isolated. Oxidation of *trans*-$[Ru^{III}(b)_2(OH)(H_2O)]^{2+}$ or *cis*-$[Ru^{II}(b')_2(H_2O)_2]^{2+}$ by electrochemical methods or by cerium(IV) in water produced the respective dioxoruthenium(VI) species (*192–195*). The diamagnetic *trans*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$ and *trans*-$[Ru^{VI}(5,5'\text{-}Me_2bpy)_2(O)_2]^{2+}$ species exhibit an intense ν_{as}(Ru=O) stretch at 850 cm^{-1}. Similar observations have also been reported for *trans*-$[Ru^{VI}(phen)_2(O)_2]^{2+}$. The UV–VIS absorption spectrum of *trans*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$ in MeCN shows a characteristic weak vibronically structured absorption band at ~400 nm, assigned as the $(d_{xy})^2 \rightarrow (d_{xy})^1(d_\pi{}^*)^1$ transition ($d_\pi{}^* = d_{xz}, d_{yz}$) (*192*). The *trans*-$[Ru^{VI}(5,5'\text{-}Me_2bpy)_2(O)_2](ClO_4)_2$ complex is a powerful oxidant with $E^0[Ru^{VI}/Ru^{IV}]$ = 1.0V vs SCE and can oxidize a wide variety of organic substrates including adamantane to adamantan-1-ol and cyclohexane to chclohexanone (*192*). The complex *trans*-$[Ru^{VI}(phen)(O)_2](ClO_4)_2$ has been found to catalyze oxidation of cyclohexene and norbornene by PhIO (*194*).

The *cis*-$[Ru^{VI}(2,9\text{-}Me_2phen)_2(O)_2]^{2+}$ and $[Ru^{VI}(6,6\text{-}Cl_2bpy)_2(O)_2]^{2+}$ complexes show two IR bands for the ν(Ru=O) stretch at 839 and 787 cm^{-1} for the former (*196*) and 840 and 790 cm^{-1} for the latter (*195*). An O—Ru—O angle of about 90° has been suggested from the IR data of *cis*-$[Ru^{VI}(2,9\text{-}Me_2phen)_2(O)_2]^{2+}$. Both *cis*-$[Ru^{VI}(2,9Me_2phen)_2(O)_2]^{2+}$ and *cis*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2(O)_2]^{2+}$ were found to be efficient oxidants for alkenes. The *cis*-$[Ru^{VI}(2,9\text{-}Me_2phen)_2(O)_2]^{2+}$ complex has been demonstrated by Drago and co-workers to epoxidize alkenes such as norbornene, cyclohexene, and *trans*-β-methylstyrene catalytically with oxygen under pressure (40 psi) at 50°C (*196*). Aerobic oxidation of methane to methanol catalyzed by *cis*-$[Ru^{VI}(2,9\text{-}Me_2phen)_2(O)_2]^{2+}$ has also been reported (*197*). The *cis*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2(O)_2]^{2+}$ complex has been shown to rapidly oxidize chloride to chlorine, tetrahydrofuran to γ-butyrolactone, cyclohexane to cyclohexanone, toluene to benzaldehyde, and alkenes to epoxides (*195*). Moreover, it has been found to be an active and robust catalyst for the electrochemical oxidation of methanol, ethanol, propan-2-ol, and tetrahydrofuran (*198*) and for the hydroxylation of saturated alkanes by *tert*-butyl hydroperoxide (*199*). A modified electrode fabricated by coating Nafion and *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ has been found to exhibit novel catalytic activities in organic oxidation (*195, 200*).

The *cis*- and *trans*-$[Os^{VI}(bpy)_2(O)_2]^{2+}$ have also been prepared. The *cis*-$[Os^{VI}(bpy)_2(O)_2]^{2+}$ complex was prepared by Ce(IV) oxidation of $[Os(bpy)_2CO_3]$, whereas *trans*-$[Os^{VI}(bpy)_2(O)_2]^{2+}$ was obtained by isomerization of the corresponding *cis*-dioxo complex (*74*). Both complexes were characterized by ^1H NMR and IR spectroscopy (*74*). As in the case of the ruthenium analog, the *cis* complex is also characterized by two ν(Os=O) stretches, symmetric and asymmetric at 883 and 863 cm^{-1}, respectively, in the IR spectrum. An O—Os—O bond angle of ~130° has been estimated from the IR spectral data.

A $[Os^{VI}(phen)(OH)_2(O)_2]\cdot 5H_2O$ complex, made by the reaction of $K_2[Os^{VI}(OH)_4(O)_2]$ and 1,10-phenanthroline (*201*), has been studied by X-ray crystallography [d(Os=O) = 1.742(4) Å, O—Os—O angle = 166.2(2)°] (*184*).

A series of *trans*-dioxoruthenium(VI) complexes of macrocyclic amine ligands, *trans*-$[Ru^{VI}(L)(O)_2]^{2+}$ (L = 14TMC, 15TMC, 16TMC, $CRMe_3$) (*30, 32, 202*), *trans*-$[Ru^{VI}(TMEA)_2(O)_2]^{2+}$ (*30*), and *trans*-$[Ru^{VI}(pytn)(O)_2]^{2+}$ (*203*) have been prepared by Che and co-workers. Reaction of *trans*-$[Ru^{III}(L)Cl_2]^+$ [L = 14TMC, 15TMC, 16TMC, $CRMe_3$,

$(TMEA)_2]$ with Ag^+ followed by subsequent oxidation by H_2O_2 gave *trans*-$[Ru^{VI}(L)(O)_2]^{2+}$, isolated as the ClO_4^- and PF_6^- salt (*30*). The X-ray crystal structures of *trans*-$[Ru^{VI}(15TMC)(O)_2](ClO_4)_2$ and *trans*-$[Ru^{VI}(16TMC)(O)_2](ClO_4)_2$ have been determined: $d(Ru{=}O)$, 1.718(5) Å for the former and 1.705(7) Å for the latter (Fig. 14) (*204*). The *trans*-$[Ru^{VI}(pytn)(O)_2]^{2+}$ complex has been similarly prepared (*203*). The IR spectral data of these complexes are listed in Table I.

The σ-saturated nature of the macrocyclic tertiary amine ligands enables the high-energy metal-localized transition to be observed (*30*). Two types of electronic transitions have been observed in the uv–vis absorption spectra of these complexes, the ligand-field ($d_{xy} \rightarrow d_\pi{}^*$) and the ligand-to-metal ($p_\pi(O) \rightarrow d_\pi(Ru)$) charge transfer (LMCT) transitions. The weak vibronic structured band at ~370–400 nm, assigned to the $(d_{xy})^2 \rightarrow (d_{xy})^1(d_\pi{}^*)^1$ transition that is vibronically coupled to the A_{2u} stretching mode of the O=Ru=O bond, is characteristic of these species, the position of which is found to be insensitive to the nature of the equatorial amine ligand as well as the macrocyclic ring size of L (Table III). This has been shown to be in accordance with the formulation that the electronic transition occurs within the nonbonding d_π

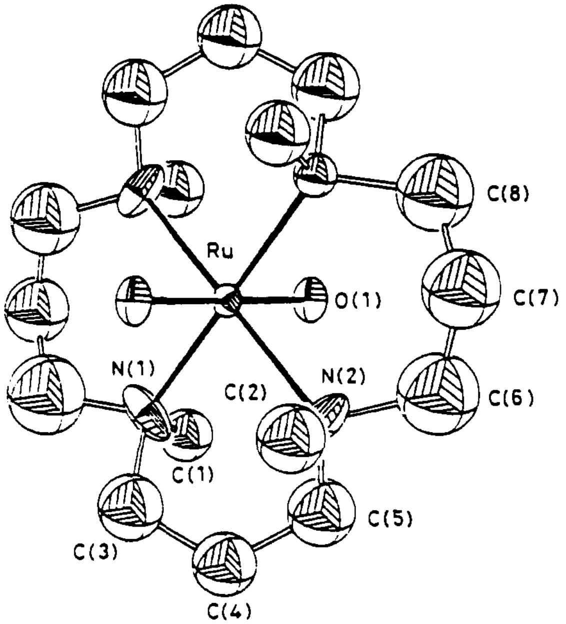


FIG. 14. A perspective view of the *trans*-$[Ru^{VI}(16TMC)(O)_2]^{2+}$ cation with atom labeling. From Ref. (*204*).

orbitals. Similar electronic absorption bands have also been found in *trans*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$ (*193*) and *trans*-$[Ru^{VI}(phen)_2(O)_2]^{2+}$ (*194*). The blue-shift of this $d_{xy} \rightarrow d_{\pi}^*$ transition in Ru(VI) relative to Ru(V) has been discussed in Section II,B,1,c. A very weak shoulder at ~430–450 nm has been suggested to arise from the singlet–triplet transition of $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{\pi}^*)^1$. The low ε value ($\simeq$50) is in accord with the small spin–orbit coupling constant of Ru. Bands in the region 220–320 nm have been assigned as the $p_{\pi}(O) \rightarrow d_{\pi}(Ru)$ LMCT transition with substantial σN(L) → Ru(VI) charge-transfer character, as evidenced by the variation of the position and the relative intensity of these bands with the nature of the equatorial amine ligand (*30, 205*).

A mixed ligand *trans*-$[Ru^{VI}(N_2O_2)(O)_2]^{2+}$ complex has been similarly prepared from the cerium(IV) oxidation of *trans*-$[Ru^{III}(N_2O_2)(OH)(OH_2)]^{2+}$ (*46*). Because of the weaker donor strength of N_2O_2, *trans*-$[Ru^{VI}(N_2O_2)(O)_2]^{2+}$ has an $E^0[Ru^{VI}/Ru^{IV}]$ = 0.92 V vs SCE, comparable to that of *trans*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$, and has been demonstrated to be an active oxidant (*46*).

Reaction of *cis*-$[Ru^{III}(Tet\text{-}Me_6)Cl_2]^+$ with $AgCF_3SO_3$ in water gave *cis*-$[Ru^{III}(Tet\text{-}Me_6)(OH)(OH_2)]^{2+}$, which could be oxidized by Ce(IV) to *cis*-$[Ru^{VI}(Tet\text{-}Me_6)(O)_2]^{2+}$ in water (*134*). The *cis*-$[Ru^{VI}(Tet\text{-}Me_6)(O)_2](ClO_4)_2$ is a green diamagnetic complex with IR bands at 874 and 855 cm^{-1}. Its structure has been characterized by X-ray crystallography: d(Ru=O) = 1.795 Å, O—Ru—O angle = 112.0(4)° (Fig. 15).

The $[Os^{VI}(O)_2(NH_3)_4]Cl_2$ complex was made from the reaction of *trans*-$[Os^{VI}(O)_2(OH)_4]K_2$ with NH_4Cl (*206*). The ethylenediamine complex *trans*-$[Os^{VI}(en)_2(O)_2]Cl_2$ is similarly made from *trans*-$[Os^{VI}(O)_2(OH)_4]K_2$ and ethylenediamine dihydrochloride (*207*); the bisulfate salt of which has been characterized by X-ray crystallography [d(Os=O) = 1.74(1) Å, O—Os—O angle = 180°] (*208*). Direct reaction of OsO_4 with a series of amino acids in aqueous solution gives *trans*-$Os(O)_2(an)_2$ (an = glycinato, DL-glycinato, DL-valinato, DL-leucinato, DL-*iso*-leucinato, and DL-phenyalaninato), and the X-ray crystal structure of *trans*-$[Os(O)_2(NH_2CH_2CO_2)_2]$ has been elucidated (*209*).

The six-coordinate *trans*-$[Os(NH_2C(Me)_2C(Me)_2NH_2)_2(O)_2]^{2+}$ and five-coordinate $[OsO\{NHC(Me)_2C(Me)_2NH\}\{NH_2C(Me)_2C(Me)_2NH\}]^+$ complexes have been prepared and found to be in equilibrium in solution (*210*). The X-ray structure of the five-coordinate square-pyramidal Os^{VI}=O complex has been determined with a measured Os=O distance of 1.72(2) Å (*210*).

Similar to the ruthenium case, a series of *trans*-dioxoosmium(VI) of macrocyclic tertiary amine ligands, *trans*-$[Os^{VI}(O)_2(L)]^{2+}$ (L = 14TMC, 15TMC, 16TMC, $CRMe_3$), have been synthesized from H_2O_2 oxidation

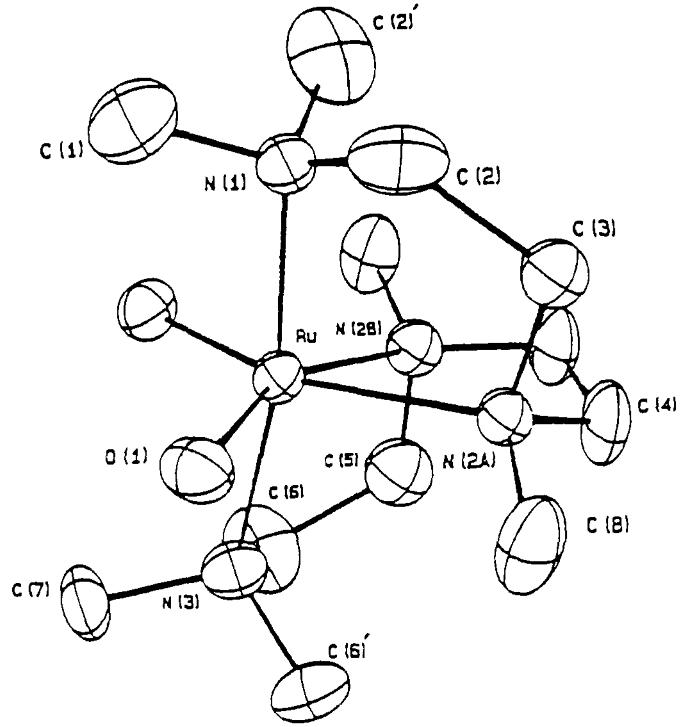


FIG. 15. ORTEP plot of *cis*-$[Ru^{VI}(Tet\text{-}Me_6)(O)_2]^{2-}$ cation with atomic numbering scheme. From Ref. (*134*).

of the Os^{III} precursors, which were prepared by refluxing an ethanolic solution of Na_2OsCl_6 and the macrocyclic amine ligands in the presence of tin plates (*75, 211*). Their IR spectral data are listed in Table I. Their UV-visible spectra are characterized by two vibronic structured electronic absorption bands centered at ~310 and 350 nm, assignable to the spin-allowed and spin-forbidden $(d_{xy})^2 \rightarrow (d_{xy})^1(d_\pi{}^*)^1$ transitions ($d_\pi{}^* = d_{xz}, d_{yz}$) (Table III). Assuming D_{4h} symmetry for the molecule, the band at ~310 and 350 nm are assigned as the respective $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow E_g(^3E_g)$ transitions, which are vibronically coupled to the $A_{2u}[\nu(Os{=}O)]$ stretch. Very weak absorptions are also observed in the low-energy tail of the low-energy band, which has been suggested to be attributed to transitions from $^1A_{1g}$ to the spin–orbit sublevels of the ^3E_g state. Similar to the ruthenium case, the relative insensitivity of the $(d_{xy})^2 \rightarrow (d_{xy})^1(d_\pi{}^*)^1$ transition to the nature of the equatorial ligands is in agreement with the lack of involvement of $d_\sigma{}^*$ electrons. The occurrence and the much higher absorption coefficients of the $^1A_{1g} \rightarrow E_g(^3E_g)$ transition for the osmium complexes over that of ruthenium, which appears as a weak shoulder at 455 nm ($\varepsilon_{max} \simeq 50$ dm^3 mol^{-1} cm^{-1}) for *trans*-$[Ru^{VI}(14TMC)(O)_2](ClO_4)_2$, have been attributed to the larger spin–orbit coupling constant for the heavier osmium atom.

The electrochemistry of both *trans*-dioxoosmium(VI) and ruthenium(VI) macrocyclic tertiary amine complexes has been studied in great detail. Both *trans*-$[Ru^{VI}(b)_2(O)_2]^{2+}$ and *trans*-$[Ru^{VI}(14TMC)(O)_2]^{2+}$ and its related complexes display similar cyclic voltammograms in aqueous solution (*132, 212*). At pH ≤ 7, three reversible/quasi-reversible redox couples, corresponding to the redox reactions are observed:

$$[Ru^{VI}(O)_2]^{2+} + 2e^- + 2H^+ \rightarrow [Ru^{IV}(O)(OH_2)]^{2+}$$

$$[Ru^{IV}(O)(OH_2)]^{2+} + e^- + H^+ \rightarrow [Ru^{III}(OH)(OH_2)]^{2+}$$

$$[Ru^{III}(OH)(OH_2)]^{2+} + e^- + H^+ \rightarrow [Ru^{II}(OH_2)_2]^{2+}$$

The two-electron Ru(VI)/Ru(IV) couple splits into two reversible one-electron couples, Ru(VI)/Ru(V) and Ru(V)/Ru(IV), at high pH (usually pH > 8):

$$[Ru^{VI}(O)_2]^{2+} + e^- \rightarrow [Ru^{V}(O)_2]^{+}$$

$$[Ru^{V}(O)_2]^{+} + e^- + H^+ \rightarrow [Ru^{IV}(O)(OH)]^{+}$$

The direct reduction of Ru(VI) to Ru(IV) in acidic medium is due to the fact that *trans*-dioxoruthenium(V) undergoes rapid acid-catalyzed disproportionation in aqueous solution (*138*),

$$2[Ru^{V}(O)_2]^{+} + 2H^+ \rightarrow [Ru^{IV}(O)(OH_2)]^{2+} + [Ru^{VI}(O)_2]^{2+},$$

the kinetics of which has been described in Section II,B,1,c. As expected, the E^0 of these proton-coupled electron-transfer redox couples shift cathodically with increase in pH in a manner governed by the Nernst equation. The Pourbaix diagrams of *trans*-$[Ru^{VI}(14TMC)(O)_2]^{2+}$ and *trans*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$ are shown in Figs. 16 and 17, respectively. In acetonitrile, *trans*-$[Ru^{VI}(L)(O)_2]^{2+}$ undergoes a reversible one-electron reduction process (*30*):

$$trans\text{-}[Ru^{VI}(L)(O)_2]^{2+} + e^- \rightarrow trans\text{-}[Ru^{V}(L)(O)_2]^{+}$$

Since *trans*-$[Ru^{VI}(b)_2(O)_2]^{2+}$ are only stable in aqueous medium, their electrochemistry in aprotic solvent such as acetonitrile has not been investigated.

The electrochemical data of *trans*-dioxoruthenium(VI) complexes are summarized in Table II. Enlargement of the hole size of macrocyclic tertiary amine from the 14- to 16-membered ring does not affect the

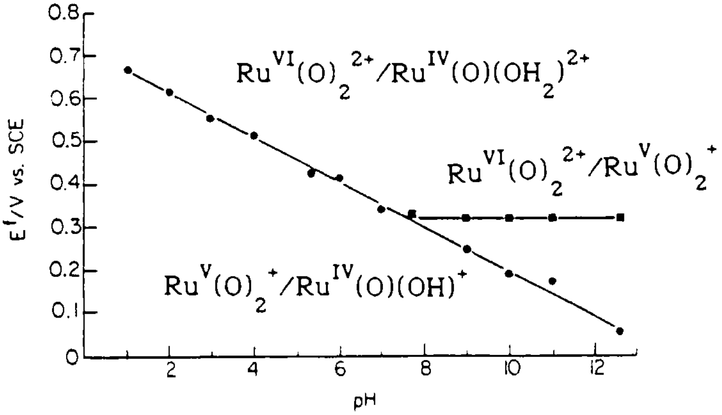


FIG. 16. Pourbaix diagram for *trans*-$[\mathrm{Ru^{VI}(14TMC)(O)_2}]^{2-}$.

$E_{1/2}$ values of *trans*-$[\mathrm{Ru^{VI}(L)(O)_2}]^{2+}$/*trans*-$[\mathrm{Ru^{IV}(L)(OH_2)}]^{2+}$ and *trans*-$[\mathrm{Ru^{VI}(L)(O)_2}]^{2+}$/*trans*-$[\mathrm{Ru^{V}(L)(O)_2}]^{+}$ redox couples. However, replacement of TMC by pyridine-containing ligands such as $\mathrm{CRMe_3}$ or π-aromatic ligands such as bpy leads to an increase in the E^0 values of

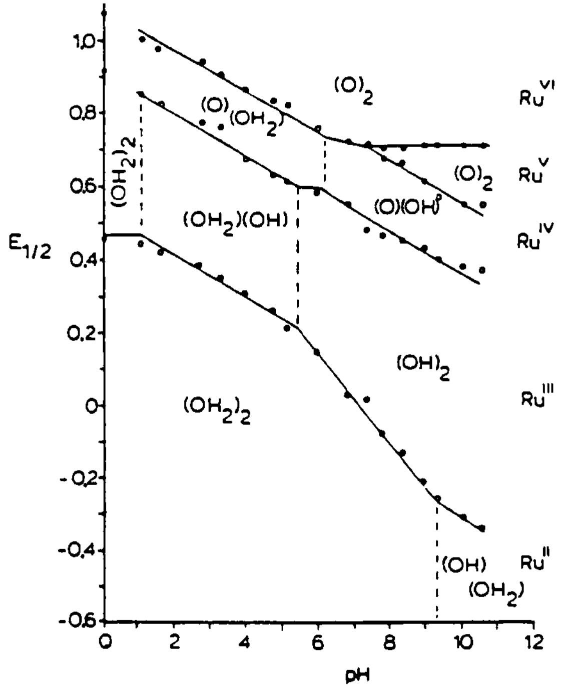


FIG. 17. Pourbaix diagram for *trans*-$[\mathrm{Ru^{VI}(bpy)_2(O)_2}]^{2-}$. From Ref. (*132*).

these complexes. In aqueous medium, *trans*-$[Ru^{VI}(14TMC)(O)_2]^{2+}$ is ~340 and 100 mV less oxidizing than *trans*-$[Ru^{VI}(bpy)_2(O)^2]^{2+}$ and *trans*-$[Ru^{VI}(CRMe_3)(O)_2]^2$, respectively. Similar ligand effects on the reduction potential of $Ru^{IV}{=}O$ complexes have also been observed.

The *trans*-dioxoosmium(VI) complexes have been found to show pH-dependent redox reactions (*74, 75, 211*). In acidic medium, the cyclic voltammogram of *trans*-$[Os^{VI}(L)(O)_2]^{2+}$ showed a reversible three-electron couple and an irreversible one-electron couple. The Pourbaix diagram of *trans*-$[Os^{VI}(14TMC)(O)_2]^{2+}$ is shown in Fig. 18, with slopes of −60 and −42 mV/pH, corresponding to the reactions

$$trans\text{-}[Os^{VI}(L)(O)_2]^{2+} + 3e^- + 3H^+ \rightarrow trans\text{-}[Os^{III}(L)(OH)(H_2O)]^{2+}$$

$$trans\text{-}[Os^{VI}(L)(O)_2]^{2+} + 3e^- + 2H^+ \rightarrow trans\text{-}[Os^{III}(L)(OH)_2]^+$$

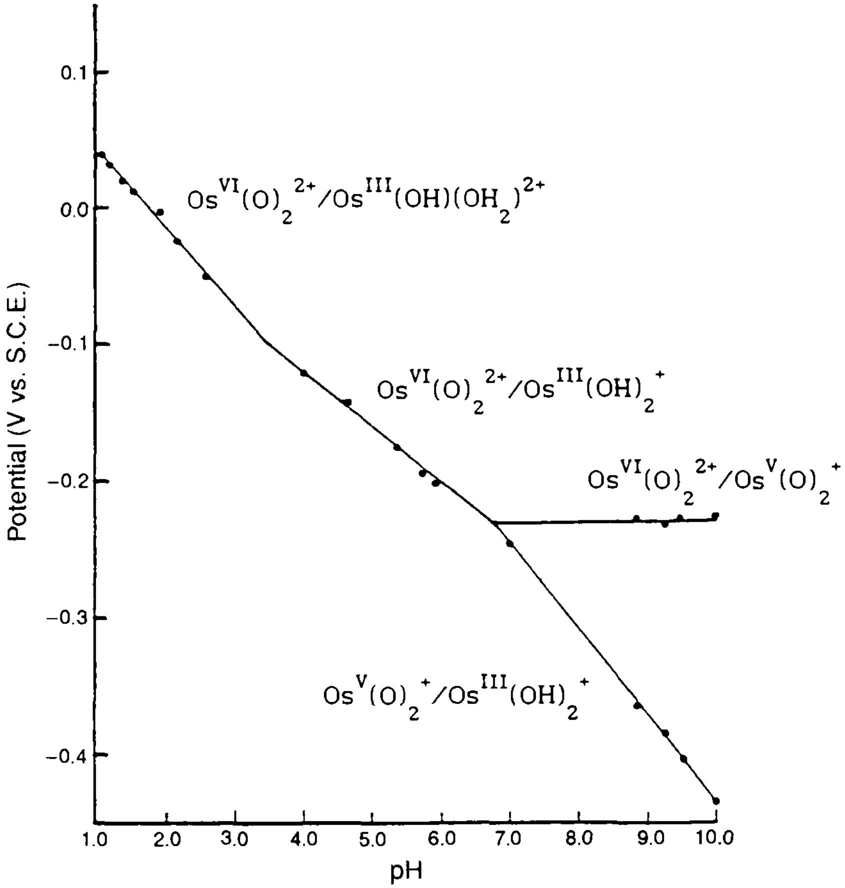


FIG. 18. Pourbaix diagram for *trans*-$[Os^{VI}(14TMC)(O)_2]^{2+}$.

As the pH is raised, the $\mathrm{Os^{VI/III}}$ couple splits into two waves corresponding to the reactions

$$\textit{trans}\text{-}[\mathrm{Os^{VI}(L)(O)_2}]^{2+} + e^- \rightarrow \textit{trans}\text{-}[\mathrm{Os^{V}(L)(O)_2}]^+$$

$$\textit{trans}\text{-}[\mathrm{Os^{V}(L)(O)_2}]^+ + 2e^- + 2\mathrm{H}^+ \rightarrow \textit{trans}\text{-}[\mathrm{Os^{III}(L)(OH)_2}]^+,$$

where L = 14TMC.

As the pH is further raised, the $\mathrm{Os^{V/III}}$ couple splits into two couples. By comparing the current magnitudes with that for the $\mathrm{Os^{VI/V}}$ couple, it is suggested that the couples correspond to two discrete one-electron tranfers and are suggested to correspond to the $\mathrm{Os^{V/IV}}$ and $\mathrm{Os^{IV/III}}$ couples. However, due to the irreversibility of these two waves and the difficulties in following the pH dependence of these two waves, no further assignment has been reported.

Proton-coupled electron-transfer reactions have also been observed for polypyridyl ruthenium and osmium oxo complexes. Meyer and coworkers also reported a reversible three-electron $\mathrm{Os^{VI/III}}$ couple with $[\mathrm{Os^{VI}(trpy)(OH)(O)_2}]^+$ (*213*) and $[\mathrm{Os^{VI}(bpy)_2(O)_2}]^{2+}$ (*74*) using an activated glassy carbon electrode. In fact, the electrochemistry for both *trans*-$[\mathrm{Os^{VI}(bpy)_2(O)_2}]^{2+}$ and *trans*-$[\mathrm{Os^{VI}(14TMC)(O)_2}]^{2+}$ are very similar. The Pourbaix diagram of *trans*-$[\mathrm{Os^{VI}(bpy)_2(O)_2}]^{2-}$ is shown in Fig. 19. It appears that the direct reduction of $\mathrm{Os^{VI}}$ to $\mathrm{Os^{III}}$ is a general

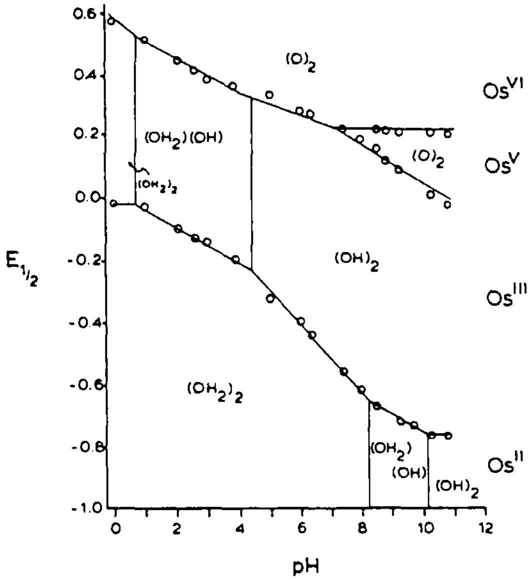


FIG. 19. Pourbaix diagram for *trans*-$[\mathrm{Os^{VI}(bpy)_2(O)_2}]^{2-}$. From Ref. (*74*).

feature of *trans*-dioxo-osmium (VI) complexes in acidic medium, provided that the intermediate Os^{V} and Os^{IV} species are stable enough with regard to dissociation and μ-oxo dimerization processes. In acetonitrile, the cyclic voltammogram of trans-$[Os^{VI}(L)(O)_2]^{2+}$ displays two reversible/quasi-reversible one-electron redox couples:

$$trans\text{-}[Os^{VI}(L)(O)_2]^{2+} + e^- \rightarrow trans\text{-}[Os^{V}(L)(O)_2]^{+}$$

$$trans\text{-}[Os^{V}(L)(O)_2]^{+} + e^+ \rightarrow trans\text{-}[Os^{IV}(L)(O)_2]$$

The change in macrocyclic ring size of L has only a slight effect on the E^0 values. However, a shift to more positive redox potential has been observed upon substitution of a tertiary nitrogen by a pyridyl group as in $CRMe_3$, attributed to the preferential stabilization of the electron-rich low-valent state of osmium by the π-acceptor ability of the pyridyl group.

cis-Dioxo-ruthenium(VI) and osmium(VI) also exhibit reversible proton-coupled electron-transfer redox couples.

In the case of *cis*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$ (*132, 133*), even at pH 1, all four couples, Ru(VI/V), Ru(V/IV), Ru(IV/III), and Ru(III/II), are observable. However, the kinetically slow Ru(IV/III) couple appears only as an oxidative shoulder and its reversibility depends on the nature of the electrode surface. At pH 1,

$$[Ru^{VI}(b)_2(O)_2]^{2+} + e^- + H^+ \rightarrow [Ru^{V}(b)_2(O)(OH)]^{2+}$$

$$[Ru^{V}(b)_2(O)(OH)]^{2+} + e^- + H^+ \rightarrow [Ru^{IV}(b)_2(O)(OH_2)]^{2+}$$

$$[Ru^{IV}(b)_2(O)(OH_2)]^{2+} + e^- + 2H^+ \rightarrow [Ru^{III}(b)_2(OH_2)_2]^{3+}\ \text{(slow)}$$

$$[Ru^{III}(b)_2(OH_2)_2]^{3+} + e^- \rightarrow [Ru^{II}(b)_2(OH_2)_2]^{2+}$$

The E^0 values of these redox couples shift cathodically with increase in pH. The Pourbaix diagram for *cis*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$ is given in Fig. 20.

Similarly, in the case of *cis*-$[Ru^{VI}(6,6\text{-}Me_2bpy)_2(O)_2]^{2+}$ (*214*) and *cis*-$[Ru^{VI}(2,9\text{-}Me_2phen)_2(O)_2]^{2+}$ (*214*) (or *cis*-$[Ru^{II}(L)_2((H_2O)_2]^{2+}$), the cyclic voltammograms in acidic medium show all four couples, though not all of them are reversible. The electrochemical steps have not been easily observed individually, the difficulties being attributed to adsorption phenomena or precipitation on the electrodes, and slow electrochemical kinetics.

With *cis*-$[Ru^{VI}(6,6\text{-}Cl_2bpy)_2(O)_2]^{2+}$, only two redox couples were observable at pH 1–3 (*200*), which has been assigned as the Ru(VI/IV) and Ru(IV/II) couples:

$$[Ru^{VI}(6,6\text{-}Cl_2bpy)_2(O)_2]^{2+} + 2e^- + 2H^+ \rightarrow [Ru^{IV}(6,6\text{-}Cl_2bpy)_2(O)(OH_2)]^{2+}$$

$$[Ru^{IV}(6,6\text{-}Cl_2bpy)_2(O)(OH_2)]^{2+} + 2e^- + 2H^+ \rightarrow [Ru^{II}(6,6\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$$

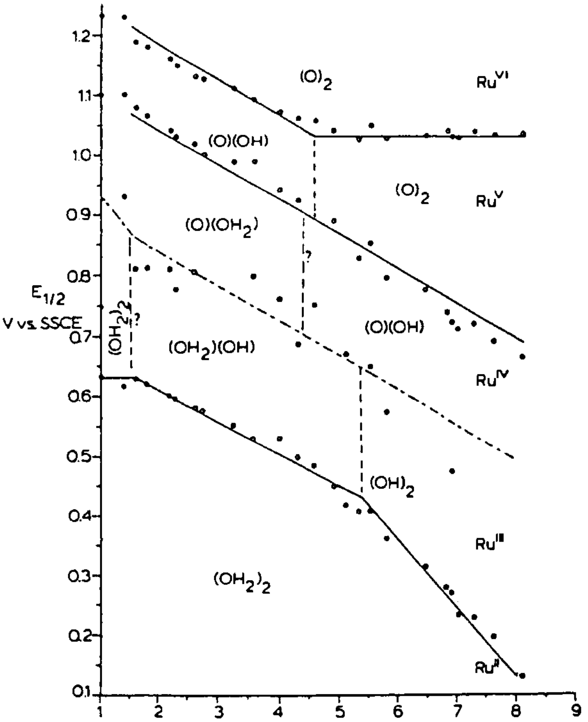


FIG. 20. Pourbaix diagram for *cis*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$. From Ref. (*132*).

The *cis*-$[Ru^{VI}(tet\text{-}Me_6)(O)_2]^{2+}$ complex has also been reported to display proton-coupled electron-transfer redox couples in aqueous medium (*134, 136*). The following electrode reactions for the couples have been observed (pH 1.0):

$$cis\text{-}[Ru^{VI}(tet\text{-}Me_6)(O)_2]^{2+} + 2e^- + 2H^+ \rightarrow cis\text{-}[Ru^{IV}(tet\text{-}Me_6)(O)(OH_2)]^{2+}, \qquad E^0 = 0.80 \text{ V}$$

$$cis\text{-}[Ru^{IV}(tet\text{-}Me_6)(O)(OH_2)]^{2+} + e^- + H^+ \rightarrow cis\text{-}[Ru^{III}(tet\text{-}Me_6)(OH)(OH_2)]^{2+}, \qquad E^0 = 0.63 \text{ V}$$

$$cis\text{-}[Ru^{III}(tet\text{-}Me_6)(OH)(OH_2)]^{2+} + e^- + H^+ \rightarrow cis\text{-}[Ru^{II}(tet\text{-}Me_6)(OH_2)_2]^{2+}, \qquad E^0 = 0.26 \text{ V}$$

The Pourbaix diagram of the formal potentials versus pH of the medium over the pH range 1 to 10 is shown in Fig. 21. At pH 2, the $Ru^{VI/IV}$ couple started to split into two quasi-reversible one-electron

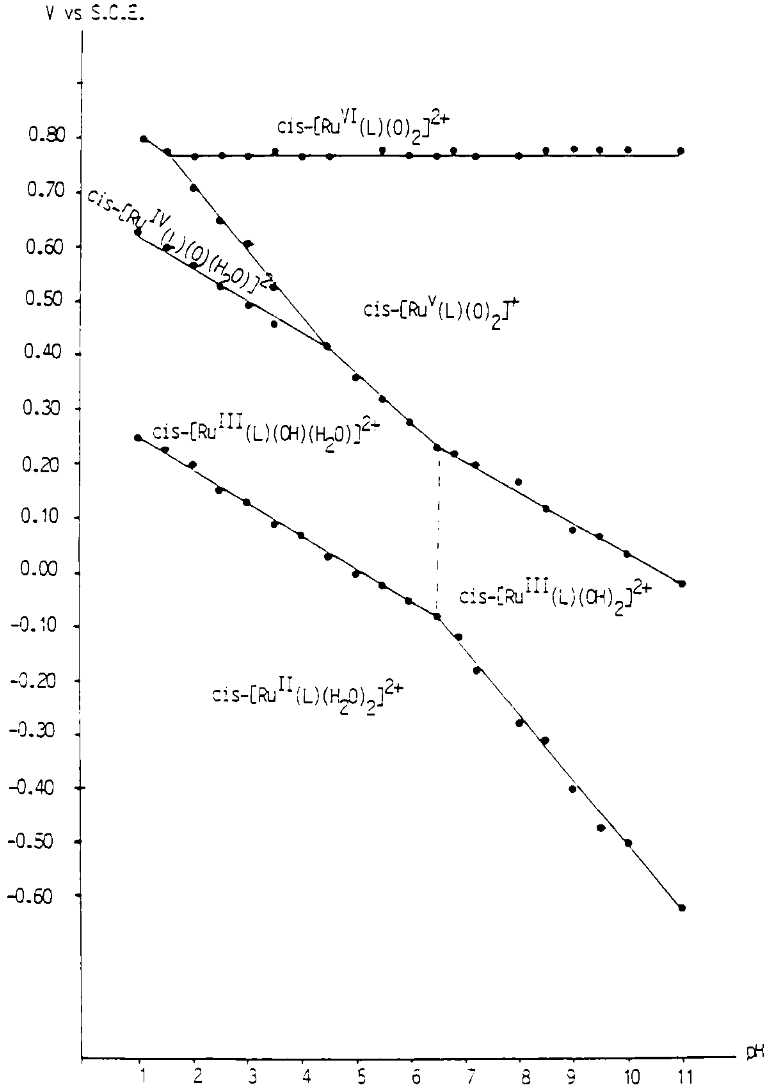


FIG. 21. Pourbaix diagram for *cis*-$[\mathrm{Ru^{VI}(Tet\text{-}Me_6)(O)_2}]^{2+}$.

couples, appearing at 0.77 and 0.71 V, which have been assigned to the $\mathrm{Ru^{VI/V}}$ and $\mathrm{Ru^{V/IV}}$ couples, respectively:

$$cis\text{-}[\mathrm{Ru^{VI}(tet\text{-}Me_6)(O)_2}]^{2+} + e^- \rightarrow cis\text{-}[\mathrm{Ru^{V}(tet\text{-}Me_6)(O)_2}]^{+}$$

$$cis\text{-}[\mathrm{Ru^{V}(tet\text{-}Me_6)(O)_2}]^{+} + e^- + 2\mathrm{H}^+ \rightarrow cis\text{-}[\mathrm{Ru^{IV}(tet\text{-}Me_6)(O)(OH_2)}]^{2+}$$

At pH 4.5, the $Ru^{V/IV}$ and $Ru^{IV/III}$ couples merge together to form a new two-electron $Ru^{V/III}$ couple:

$$cis\text{-}[Ru^{V}(tet\text{-}Me_6)(O)_2]^+ + 2e^- + 3H^+ \rightarrow cis\text{-}[Ru^{III}(tet\text{-}Me_6)(OH)(OH_2)]^{2+}$$

Unlike trans-dioxoruthenium(VI) complexes such as *trans*-$[Ru^{VI}(L)(O)_2]^{2+}$ (L = 14TMC, N_2O_2 or pytn) (*46, 203, 212*) and *trans*-$[Ru^{VI}(b)_2(O)_2]^{2+}$ (*132, 193*), which have similar electrode reactions, *cis*-$[Ru^{VI}(tet\text{-}Me_6)(O)_2]^{2+}$ is quite distinct from other *cis*-dioxoruthenium(VI) systems such as *cis*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$ in that both the Ru^{V} and the Ru^{IV} species are unstable with respect to disproportionation. The *cis*-$[Ru^{V}(tet\text{-}Me_6)(O)_2]^+$ complex has been isolated and is found to disproportionate in strongly acidic medium:

$$cis\text{-}[Ru^{V}(tet\text{-}Me_6)(O)_2]^+ + cis\text{-}[Ru^{V}(tet\text{-}Me_6)(O)(OH)]^{2+} \rightleftharpoons cis\text{-}[Ru^{VI}(tet\text{-}Me_6)(O)_2]^{2+} + cis\text{-}[Ru^{IV}(tet\text{-}Me_6)(O)(OH)]^+$$

The disproportionation equilibrium constant K_{disp} has been estimated to be 10.34 ($\Delta G_{disp}{}^0 = -5.79$ kJ mol^{-1}), which is small compared to a K_{disp} of 3.2×10^{11}, found in *trans*-$[Ru^{V}(14TMC)(O)_2]^+$.

In acetonitrile, a reversible one-electron reduction couple, corresponding to the $Ru^{VI/V}$ couple, is observed at 0.53 V vs $Ag/AgNO_3$ (0.1 *M* in MeCN) (*136*), similar to that found in other trans-dioxoruthenium(VI) systems:

$$cis\text{-}[Ru^{VI}(tet\text{-}Me_6)(O)_2]^{2+} + e^- \rightarrow cis\text{-}[Ru^{V}(tet\text{-}Me_6)(O)_2]^+$$

Since other *cis*-dioxoruthenium(VI) complexes such as *cis*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$ have not been isolated and are very unstable in organic solvents, their electrochemistry in acetonitrile has not been explored.

For the *cis*-$[Os^{VI}(bpy)_2(O)_2]^{2+}$ complex, three couples were observed at pH 1, namely the Os(VI/V), Os(V/III), and Os(III/II) couples (*74*). The Os (V/III) couple separates into two resolvable one-electron waves at pH 4, corresponding to the Os(V/IV) and Os(IV/III) couples. The Pourbaix diagram for *cis*-$[Os^{VI}(bpy)_2(O)_2]^{2+}$ is shown in Fig. 22.

A comparative summary of reduction potentials for the *cis* and *trans* couples at various pH values has been made. There is a preferential electronic stabilization of the trans-dioxo $(d_\pi)^2$ structure in *trans*-$[M^{VI}(bpy)_2(O)_2]^{2+}$ and trans-$[M^{VI}(tetraamine)(O)_2]^{2+}$ relative to the corresponding *cis* isomers (*74, 132, 134*). These observations have been explained in terms of both electronic effects and differences in solvation energies. Effects arising from differences in solvation energies have been suggested to be slight. The *cis–trans* electronic effect has been rationalized on the basis of simple molecular orbital arguments. For the trans-dioxo species, the d_π orbital ordering is $d_{xy} < d_{xy}, d_{yz}$ taking

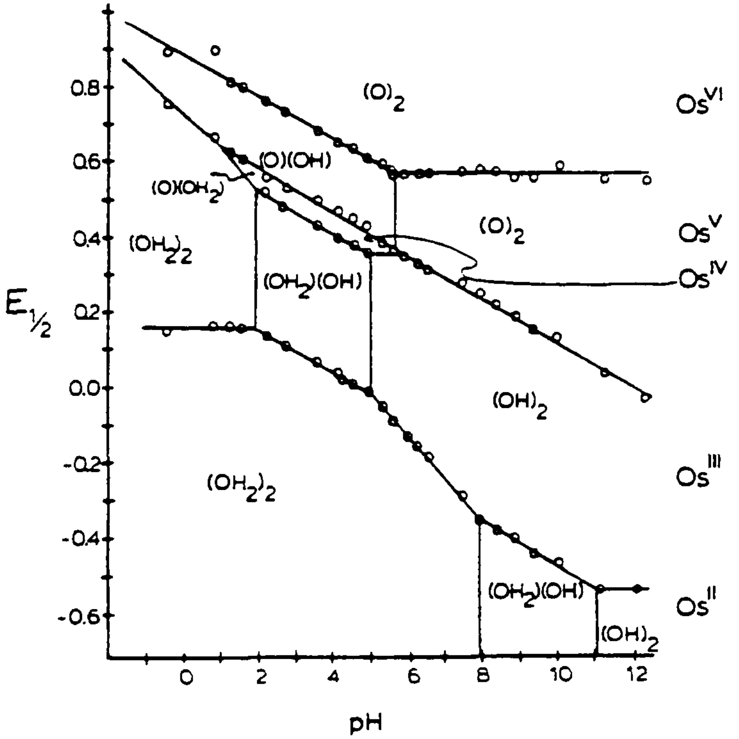


FIG. 22. Pourbaix diagram for *cis*-$[Os^{VI}(bpy)_2(O)_2]^{2-}$. From Ref. (*74*).

the z axis to lie along the O═Os═O bond axis. The affinity of trans-dioxoosmium(VI) $[(d_{xy})^2]$ for an additional electron to give Os(V) $[(d_{xy})^1(d_\pi{}^*)^1]$ is expected to be decreased by the considerable antibonding character of d_{xz}, d_{yz} arising from $d_\pi{}^*(\mathrm{Os})$-$p_\pi(\mathrm{O})$ mixing. On the other hand, the d_π orbital ordering in the *cis* isomer is $d_{xy}, d_{yz} < d_{xy}$, or given its diamagnetism $d_{\pi 1} < d_{\pi 2} \ll d_{xy}$ with the ground-state electronic configuration $(d_{\pi 1})^2$, where $d_{\pi 1}$ and $d_{\pi 2}$ are taken as if constructed from linear combinations of d_{xz} and d_{yz} including spin–orbit coupling. Electronic destabilization effects in the reduction of Os(VI) to Os(V) are smaller since the $d_{\pi 1}$–$d_{\pi 2}$ energy separation is relatively small. Similar findings have also been observed in the ruthenium analogs.

The *trans*-$[Ru^{VI}(14TMC)(O)_2]^{2+}$ and *trans*-$[Ru^{VI}(16TMC)(O)_2]^{2+}$ complexes are not capable of oxidizing substrates at appreciable rates at room temperature. Modifications on the ligand environment have been made to produce macrocyclic Ru═O complexes of sufficiently high redox potentials to become active oxidants. For example, replacement of tertiary nitrogen atom by a pyridyl unit in the tetraazamacrocyclic ligands has been shown to enhance the redox potential and reactivities of the ruthenium oxidant. Tables IV, V, and VI summarize the second-order rate constants for the oxidation of benzyl alcohol to benzaldehyde (*215*), propan-2-ol to acetone (*215*), and tetrahydrofuran to γ-butyrolactone (*216*) by different trans-dioxoruthenium(VI) species, respectively. In general, the rate of oxidation was found to increase with an increase in the redox potential of the $\mathrm{Ru^{VI/IV}}$ couple. A linear free-energy plot with a slope close to the theoretical value for a two-electron transfer (i.e., 16.8 V^{-1}) has been obtained in each case. For the oxidation of benzyl alcohol, the kinetic isotope effects range from 15 to 19, and do not appear to have any correlation with the E^0 values of the Ru(VI/IV) couple (*215*). A mechanism involving hydride abstraction or an initial hydrogen atom abstraction followed by rapid in-cage electron transfer was suggested to be responsible for the oxidation reactions. Oxidation of toluene, ethylbenzene, and cumene by *trans*-$[\mathrm{Ru^{VI}(N_2O_2)(O)_2}]^{2+}$ in MeCN has also been found to proceed with large kinetic isotope effect (k_H/k_D = 16 for ethylbenzene). The second-order rate constants for ethylbenzene and cumene are similar but are substantially higher than that for toluene (*216*). Representative kinetic data for the oxidation of ethylbenzene, cumene, and toluene are collected in Table VII.

TABLE IV

REPRESENTATIVE KINETIC DATA FOR THE OXIDATION OF BENZYL ALCOHOL BY RUTHENIUM OXO COMPLEXES

Complex	At 298 K $k_2(M^{-1}\ s^{-1})$	k_H/k_D	$\Delta H\ddagger$/kcal mol^{-1} ($\Delta S\ddagger$/eu)	Ref.
trans-$[\mathrm{Ru^{VI}(14TMC)(O)_2}]^{2+}$	1.98×10^{-4} (H_2O)	—	—	*215*
trans-$[\mathrm{Ru^{VI}(TMEA)_2(O)_2}]^{2+}$	4.99×10^{-4} (H_2O)	—	—	*215*
trans-$[\mathrm{Ru^{VI}(CRMe_3)(O)_2}]^{2+}$	3.25×10^{-3} (H_2O)	18 ± 2	—	*215*
trans-$[\mathrm{Ru^{VI}(pytn)(O)_2}]^{2+}$	9.30×10^{-1} (H_2O)	15 ± 2	—	*215*
trans-$[\mathrm{Ru^{VI}(N_2O_2)(O)_2}]^{2+}$	6.85×10^{-1} (H_2O)	19 ± 2	10 (−26)	*215*
trans-$[\mathrm{Ru^{VI}(bpy)_2(O)_2}]^{2+}$	2.08×10^{1} (H_2O)	17 ± 2	—	*215*
trans-$[\mathrm{Ru^{VI}(5,5'Me_2bpy)_2(O)_2}]^{2+}$	3.59 (H_2O)	19	8.3 (−23)	*192*

TABLE IV (*Continued*)

Complex	At 298 K $k_2(M^{-1}\ s^{-1})$	k_H/k_D	$\Delta H\ddagger$/kcal mol^{-1} ($\Delta S\ddagger$/eu)	Ref.
$[Ru^V(N_4O)(O)]^{2+}$	1.2×10^2 (0.1 *M* $HClO_4$)	5.9	9.1 (−18)	*142*
trans-$[Ru^V(14TMC)(O)(NCO)]^{2+}$	1.40×10^2 (CH_3CN)	4.1	—	*139*
trans-$[Ru^V(14TMC)(O)Cl]^{2+}$	2.1×10^2 (CH_3CN)	—	—	*139*
cis-$[Ru^V(pyen)(O)Cl]^+$	8.4×10^4 (H_2O)	—	—	*140*
$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$	2.43 (0.1 *M* $HClO_4$)	50	5.7 (−38)	*51*
	1.54 (CH_3CN)		5.8 (−38)	*51*
$[Ru^{IV}(trpy)(6,6'-Cl_2bpy)(O)]^{2+}$	2.23 (0.1 *M* $HClO_4$)	39	—	*29*
$[Ru^{IV}(trpy)(TMEA)(O)]^{2+}$	2.4×10^{-2} (0.1 *M* $HClO_4$)	—	—	*28*
$[Ru^{IV}(bpy)_2(PEt_3)(O)]^{2+}$	9.2×10^{-2} (H_2O)	—	—	*53*
	2.8×10^{-1} (MeCN)	—	—	*53*
	2.5×10^{-1} (CH_2Cl_2)	—	—	*53*
$[Ru^{IV}(bpy)_2(PPh_3)(O)]^{2+}$	1.05 (H_2O)	—	—	*53*
	8.3×10^{-1} (MeCN)	—	—	*53*
	5.5×10^{-1} (CH_2Cl_2)	—	—	*53*
$[Ru^{IV}(bpy)_2(AsPh_3)(O)]^{2+}$	6.8×10^{-1} (MeCN)	—	—	*53*
	5.8×10^{-1} (CH_2Cl_2)	—	—	*53*
$[Ru^{IV}(bpy)(biq)(PEt_3)(O)]^{2+}$	4.07×10^{-2} (H_2O)	—	—	*27*
	3.22×10^{-1} (CH_2Cl_2)	—	—	*27*
$[Ru^{IV}(bpy)(biq)(PMe_3)(O)]^{2+}$	6.62×10^{-1} (H_2O)	—	—	*27*
	5.35×10^{-1} (CH_2Cl_2)	—	—	*27*
$[Ru^{IV}(bpy)(biq)(PPh_3)(O)]^{2+}$	2.23 (H_2O)	—	—	*27*
	6.44×10^{-1} (CH_2Cl_2)	—	—	*27*

TABLE V

REPRESENTATIVE KINETIC DATA FOR THE OXIDATION OF PROPAN-2-OL BY RUTHENIUM OXO COMPLEXES

Complex	At 298 K $k_2(M^{-1}\ s^{-1})$	k_H/k_D	$\Delta H‡$/kcal mol^{-1} ($\Delta S‡$/eu)	Ref.
trans-[Ru^{VI}(bpy)$_2$(O)$_2$]$^{2+}$	2.0 (H$_2$O)	—	—	*215*
trans-[Ru^{VI}(N$_2$O$_2$)(O)$_2$]$^{2+}$	4.6×10^{-2} (H$_2$O)	11	12 (−28)	*215*
	1.5×10^{-2} (MeCN)		—	*215*
trans-[Ru^{VI}(pytn)(O)$_2$]$^{2+}$	1.9×10^{-2} (H$_2$O)	—	—	*215*
[Ru^{V}(N$_4$O)(O)]$^{2+}$	13.5 (0.1 *M* HClO$_4$)	5.3	9.2 (−22)	*142*
[Ru^{IV}(bpy)$_2$(py)(O)]$^{2+}$	6.7×10^{-2} (H$_2$O)	18	9 (−34)	*51*
	8.7×10^{-3} (MeCN)		8 (−42)	*51*
[Ru^{IV}(bpy)$_2$(PEt$_3$)(O)]$^{2+}$	1.35×10^{-3} (MeCN)	—	—	*53*
	2.3×10^{-3} (CH$_2$Cl$_2$)	—	—	*53*
[Ru^{IV}(bpy)$_2$(PPh$_3$)(O)]$^{2+}$	2.3×10^{-3} (H$_2$O)	—	—	*53*
[Ru^{IV}(trpy)(6,6′-Cl$_2$bpy)(O)]$^{2+}$	7.7×10^{-3} (MeCN)	—	—	*29*
[Ru^{IV}(trpy)(TMEA)(O)]$^{2+}$	4.3×10^{-3} (MeCN)	—	—	*28*

The kinetics of oxidation of alkenes by *trans*-[Ru^{VI}(14TMC)(O)$_2$]$^{2+}$, *trans*-[Ru^{VI}(CRMe$_3$)(O)$_2$]$^{2+}$, *trans*-[Ru^{VI}(pytn)(O)$_2$]$^{2+}$, and *trans*-[Ru^{VI}(N$_2$O$_2$)(O)$_2$]$^{2+}$ with E^0[Ru(VI/V)] ranging from 0.23 to 0.70 V vs SCE have been investigated in acetonitrile (*217*). The experimental rate law is rate $= k$[Ru(VI)][alkene]. The rate constants k depend on the E^0 of the ruthenium oxidant as well as the oxidation potentials and structures of the alkenes. Representative kinetic data for the oxidation of styrene are summarized in Table VIII. For the oxidation of *para*-substituted styrenes, a linear Hammett plot of $\log K_2$ versus σ^+ of *para*-substituents with a ρ value of -2.1 was found. A charge-transfer mechanism involving preassociation of the reactants has been suggested to play an important role in the rate determining step of the oxidation.

The *cis*-[Ru^{VI}(tet-Me$_6$)(O)$_2$]$^{2+}$ complex has also been shown to exhibit stoichiometric oxidative properties, capable of oxidizing a variety of

TABLE VI

REPRESENTATIVE KINETIC DATA FOR THE OXIDATION OF TETRAHYDROFURAN BY RUTHENIUM OXO COMPLEXES

Complex	At 298 K $k_2(M^{-1}\ s^{-1})$	k_H/k_D	$\Delta H^{\ddagger}$/kcal mol^{-1} ($\Delta S^{\ddagger}$/eu)	Ref.
trans-$[Ru^{VI}(CRMe_3)(O)_2]^{2+}$	4.2×10^{-3} (0.1 M CF_3SO_3H)	—	14 (−28)	*216*
trans-$[Ru^{VI}(pyen)(O)_2]^{2+}$	1.2×10^{-2} (0.1 M CF_3SO_3H)	—	—	*216*
trans-$[Ru^{VI}(N_2O_2)(O)_2]^{2+}$	0.17 (0.1 M CF_3SO_3H)	20	10 (−28)	*216*
trans-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$	3.5 (0.1 M CF_3SO_3H)	—	—	*216*
$[Ru^{V}(N_4O)(O)]^{2+}$	31 (0.1 M $HClO_4$)	6	11.4 (−14)	*142*
RuO_4	4.3×10^{-2} (1.49 M $HClO_4$)	1.5	14 (−18)	*315*

TABLE VII

REPRESENTATIVE KINETIC DATA FOR THE OXIDATION OF ETHYLBENZENE, CUMENE, AND TOLUENE BY RUTHENIUM OXO COMPLEXES

Complex	At 298 K $k_2(M^{-1}\ s^{-1})$	k_H/k_D	$\Delta H^{\ddagger}$/kcal mol^{-1} ($\Delta S^{\ddagger}$/eu)	Ref.
Ethylbenzene				
trans-$[Ru^{VI}(pytn)(O)_2]^{2+}$	1.32×10^{-3} (MeCN)	12	13 (−24)	*216*
trans-$[Ru^{VI}(N_2O_2)(O)_2]^{2+}$	1.98×10^{-3} (MeCN)	16	14 (−22)	*216*
trans-$[Ru^{VI}(TPP)(O)_2]$	2.2×10^{-4} (CH_2Cl_2/MeOH, 19:1)	—	—	*68*
Cumene				
trans$[Ru^{VI}(pytn)(O)_2]^{2+}$	1.96×10^{-3} (MeCN)	—	14 (−25)	*216*
trans-$[Ru^{VI}(N_2O_2)(O)_2]^{2+}$	2.9×10^{-3} (MeCN)	—	11 (−31)	*216*
trans-$[Ru^{VI}(TPP)(O)_2]$	3.16×10^{-4} (CH_2Cl_2/MeOH, 19:1)	—	—	*68*
$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$	2.6×10^{-2} (MeCN)	—	—	*52*
Toluene				
trans-$[Ru^{VI}(N_2O_2)(O)_2]^{2+}$	1.8×10^{-5} (MeCN)	—	—	*216*
$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$	5×10^{-5} (MeCN)	—	—	*52*

TABLE VIII

REPRESENTATIVE KINETIC DATA FOR THE OXIDATION OF STYRENE BY RUTHENIUM OXO COMPLEXES

Complex	At 298 K $k_2(M^{-1}\ \mathrm{s}^{-1})$	$\Delta H^{\ddagger}$/kcal mol^{-1} ($\Delta S^{\ddagger}$/eu)	Ref.
trans-$[\mathrm{Ru^{VI}(14TMC)(O)_2}]^{2+}$	1×10^{-6} (MeCN)	—	*217*
trans-$[\mathrm{Ru^{VI}(CRMe_3)(O)_2}]^{2+}$	1.5×10^{-5} (MeCN)	15 (−24)	*217*
trans-$[\mathrm{Ru^{VI}(pytn)(O)_2}]^{2+}$	9.2×10^{-2} (MeCN)	12 (−24)	*217*
trans-$[\mathrm{Ru^{VI}(N_2O_2)(O)_2}]^{2+}$	2.1×10^{-1} (MeCN)	11 (−22)	*217*
trans-$[\mathrm{Ru^{VI}(TPP)(O)_2}]$	4.3×10^{-3} ($\mathrm{CH_2Cl_2}$/MeOH, 19:1)	10 (−35)	*68*
trans-$[\mathrm{Ru^{VI}(OEP)(O)_2}]$	1.55×10^{-3} ($\mathrm{ClCH_2CH_2Cl}$)	16 (−18)	*68*
$[\mathrm{Ru^{IV}(bpy)_2(py)(O)}]^{2+}$	1.48×10^{-2} (MeCN)	7.2 (−43)	*55*
$[\mathrm{Ru^{IV}(trpy)(6,6'\text{-}Cl_2bpy)(O)}]^{2+}$	2.8×10^{-2} (MeCN)	11.1 (−28.2)	*29*
$[\mathrm{Ru^{IV}(trpy)(TMEA)(O)}]^{2+}$	2.0×10^{-2} (0.1 M $\mathrm{HClO_4}$)	—	*28*
$[\mathrm{Ru^{IV}(bpy)_2(PEt_3)(O)}]^{2+}$	3.7×10^{-3} (MeCN)	15.6 (−15.9)	*43*
	4.3×10^{-3} ($\mathrm{CH_2Cl_2}$)	9.7 (−36.7)	*43*
$[\mathrm{Ru^{IV}(bpy)_2(PPh_3)(O)}]^{2+}$	8.9×10^{-3} (MeCN)	13.1 (−22.5)	*43*
	9.1×10^{-3} ($\mathrm{CH_2Cl_2}$)	13.3 (−23.4)	*43*

organic substrates (*134*). Adamantane was selectively oxidized at the tertiary C—H position. Its reactions with styrene, *cis*- and *trans*-stilbene, and cyclooctene are similar to that found for other Ru=O systems in that epoxidation and oxidative cleavage of the C=C bond were observed. No diol product was found. Preliminary kinetic studies of the oxidation of organic substrates by *cis*-$[\mathrm{Ru^{VI}(Tet\text{-}Me_6)(O)_2}]^{2+}$ revealed the following rate law: rate = k[Ru][substrate] (*136*).

The *trans*-$[\mathrm{Os^{VI}(L)(O)_2}]^{2+}$ complexes [L = 14TMC, 15TMC, 16TMC, $\mathrm{(TMEA)_2}$, $\mathrm{CRMe_3}$] have been shown to exhibit room temperature photoluminescence both in the solid state and in fluid solution (*172–174*). Excitation into the $^1A_{1g} \rightarrow {}^1E_g$ or $^1A_{1g} \rightarrow {}^3E_g$ transition of *trans*-$[\mathrm{Os^{VI}(L)(O)_2}]^{2+}$ at $\lambda > 350$ nm results in phosphorescence in the 600- to 700-

nm region. The emitting state has been assigned to be the $[(d_{xy})^1(d_\pi{}^*)^1]$ triplet state ($d_\pi{}^* = d_{xy},d_{yz}$). The photophysical properties are summarized in Table IX. These complexes have been shown to be powerful oxidants in the excited state, capable of oxidizing a wide variety of organic substrates. An excited-state redox potential of 2.3 V vs NHE, based on quenching studies with aromatic hydrocarbons, has been reported for *trans*-$[Os^{VI}(TMC)(O)_2]^{2+}$. Moreover, upon light excitation, the Os=O bond is weakened [the ν(Os—O) stretching frequency in the excited state is ~750 cm^{-1}] and photo-induced oxygen atom transfers to PPh_3, alkenes, and dialkyl sulfide have been reported.

trans-Dioxoruthenium(VI) and -osmium(VI) of porphyrin ligands have also been isolated. Groves and Quinn first isolated the *trans*-$[Ru^{VI}(TMP)(O)_2]$ complex by oxidation of [Ru(TMP)CO] with mCPBA in dichloromethane or benzene (*218*). This ruthenium complex was shown to catalyze the aerobic epoxidation of simple alkenes (*219*) and cholest-5-ene derivatives with nearly complete β-stereospecificity (*220*). Later, a series of *trans*-$[Ru^{VI}(P)(O)_2]$ complexes (P = *p*-X-TPP, OEP) of nonsterically bulky porphyrin ligands prepared by mCPBA oxidation of $[Ru^{II}(P)(CO)]$ in alcohol was also reported (*67*). A $\nu_{as}(RuO_2)$ stretch at 821 cm^{-1} has been observed. The *trans*-$[Ru^{VI}(P)(O)_2]$ are found to be active stoichiometric oxidants of alkenes and hydrocarbons, the kinetics of which have been studied. Stereoretentive epoxidation of trans- and *cis*-stilbenes by $[Ru^{VI}(TPP)(O)_2]$ has been observed, whereas the reaction between $[Ru^{VI}(OEP)(O)_2]$ and *cis*-stilbene gave a mixture of *cis*- and *trans*-stilbene oxides. Adamantane and methylcyclohexane were hydroxylated at the tertiary C—H position (*67*). The reaction of alkenes with $[Ru^{VI}(P)(O)_2]$ in a dichloromethane : methanol (19 : 1, v/v)

TABLE IX

PHOTOPHYSICAL DATA OF SELECTED OSMIUM(VI) OXO AND NITRIDO COMPLEXES IN ACETONITRILE AT ROOM TEMPERATURE

Complex	λ_{max}(Em)/nm	Lifetime, $\tau_0/\mu s$	Ref.
trans-$[Os^{VI}(14TMC)(O)_2](ClO_4)_2$	620	1.0[a]	*172*
trans-$[Os^{VI}(15TMC)(O)_2](ClO_4)_2$	625	1.0[a]	*172*
trans-$[Os^{VI}(16TMC)(O)_2](ClO_4)_2$	600	1.56[a]	*172*
trans-$[Os^{VI}(CRMe_3)(O)_2](ClO_4)_2$	710	0.88[a]	*172*
trans-$[Os^{VI}(CN)_4(O)_2](Ph_4As)_2$	710	0.40[a]	*172*
$[Os^{VI}(CN)_5(N)](Ph_4As)_2$	550	2.49[b]	*275*
$[Os^{VI}(NH_3)_4(N)](CF_3SO_3)_3$	545	1.56[b]	*276*

[a] Concentration of osmium complex $\simeq 10^{-3}$ mol dm^{-3}.

[b] Extrapolated from the plot of $1/\tau$ versus [Os(VI)≡N].

mixture has been shown to follow second-order kinetics with the following rate law: rate = $k[\mathrm{Ru}^{\mathrm{VI}}(\mathrm{P})(\mathrm{O})_2][\text{alkene}]$ under pseudo-first-order conditions, $[\text{alkene}] \gg [\mathrm{Ru}^{\mathrm{VI}}(\mathrm{P})(\mathrm{O})_2]$. A linear free-energy plot of log k versus $E_{1/2}$ (one-electron oxidation potential of alkenes) for the oxidation of various alkenes by $[\mathrm{Ru}^{\mathrm{VI}}(\mathrm{TPP})(\mathrm{O})_2]$ has been obtained (*68*). The observed slope of $-1.1\ \mathrm{V}^{-1}$ shows that there is little degree of charge transfer in the transition state. Oxidation of cyclohexene by $[\mathrm{Ru}^{\mathrm{VI}}(\mathrm{TPP})(\mathrm{O})_2]$ occurred at the allylic C—H bond with a kinetic isotope effect of 11.7 (*68*).

The *trans*-$[\mathrm{Os}^{\mathrm{VI}}(\mathrm{P})(\mathrm{O})_2]$ complex has also been synthesized by mCPBA oxidation of $[\mathrm{Os}^{\mathrm{II}}(\mathrm{P})(\mathrm{CO})]$ (*221, 222*). The X-ray crystal structure of $[\mathrm{Os}(p\text{-Me-TPP})(\mathrm{O})_2]$ has been determined with an Os=O distance of 1.743(3) Å (*221*). An extended Hückel calculation has been performed on $[\mathrm{Os}^{\mathrm{VI}}(\mathrm{P})(\mathrm{O})_2]$ (*223*). The reactivities of *trans*-$[\mathrm{Os}^{\mathrm{VI}}(\mathrm{P})(\mathrm{O})_2]$ with triphenylphosphine have also been studied. Both $[\mathrm{Os}^{\mathrm{VI}}(\mathrm{OEP})(\mathrm{O})_2]$ and $[\mathrm{Os}^{\mathrm{VI}}(\mathrm{TPP})(\mathrm{O})_2]$ react with PPh_3 to give $[\mathrm{Os}^{\mathrm{II}}(\mathrm{P})(\mathrm{OPPh}_3)]$ (P = TPP, OEP), the crystal structures of which have been determined (*224*). The photophysics and photochemistry of *trans*-$[\mathrm{Os}(\mathrm{OEP})(\mathrm{O})_2]$ have also been reported (*225*). The complex $[\mathrm{Os}(\mathrm{OEP})(\mathrm{O})_2]$ shows emission with origin at 729 nm ($\tau_0 < 6\ \mu\mathrm{s}$) and a $\phi_{\mathrm{p}} \simeq 5 \times 10^{-3}$ at 300 K in deoxygenated acetone.

trans-Dioxoosmium(VI) complexes of pyridine-amide-type ligands have also been isolated. Both *trans*-$[\mathrm{Os}^{\mathrm{VI}}(\mathrm{bpb})(\mathrm{O})_2]$ and *trans*-$[\mathrm{Os}^{\mathrm{VI}}(\mathrm{H}_2\mathrm{bpb})(\mathrm{O})_2]^{2+}$ complexes have been synthesized (*226*). The *trans*-$[\mathrm{Os}^{\mathrm{VI}}(\mathrm{H}_2\mathrm{bpb})(\mathrm{O})_2]\mathrm{Cl}_2$ complex has been prepared from the reaction of $\mathrm{K}_2[\mathrm{Os}^{\mathrm{VI}}(\mathrm{OH})_4(\mathrm{O})_2]$ with $\mathrm{H}_2\mathrm{bpb}$ in MeOH–HCl (2 *M*). Treatment of *trans*-$[\mathrm{Os}^{\mathrm{VI}}(\mathrm{H}_2\mathrm{bpb})(\mathrm{O})_2]\mathrm{Cl}_2$ with $\mathrm{Et}_3\mathrm{N}$ in MeOH gave *trans*-$[\mathrm{Os}^{\mathrm{VI}}(\mathrm{bpb})(\mathrm{O})_2]$. A trans-dioxoosmium(VI) complex of chiral tetradentate binaphthyl bis-amide ligand has been isolated (*227*). Stirring the *R*(−) or *S*(+) form of the amide ligand with $\mathrm{K}_2[\mathrm{OsO}_2(\mathrm{OH})_4]$ in methanol at 40°C for 1 h gave the respective *R* or *S* form of the orange trans-dioxoosmium(VI) product in high yield (90%). The *R* form has been established by X-ray crystallography (Fig. 23) (*227*). The osmium atom is six-coordinated with the two oxo groups *trans* to each other. However, the measured O—Os—O angle of 166.7(2)° significantly deviates from 180°. The measured Os=O distances of 1.726(6) and 1.727(5) Å are in the normal range expected for trans-dioxoosmium(VI) complexes.

trans-Dioxoosmium(VI) complexes of Schiff base ligands (salen, 5-*i*-Pr-salen, 5-*t*-Bu-salen, 3-*t*-Bu-saltmen, 5-(3-Me)-Bu-saltmen, 5-*t*-Bu-saltmen) have also been prepared by the reaction of $\mathrm{K}_2[\mathrm{Os}(\mathrm{OH})_4(\mathrm{O})_2]$ with the ligand in methanol (*228, 229*). The X-ray crystal structure of *trans*-$[\mathrm{Os}^{\mathrm{VI}}(3\text{-}t\text{-Bu-saltmen})(\mathrm{O})_2]$ has been determined: $d(\mathrm{Os{=}O})$ = 1.760(7) and 1.722(8) Å, O—Os—O angle = 176.6(4)°. These complexes

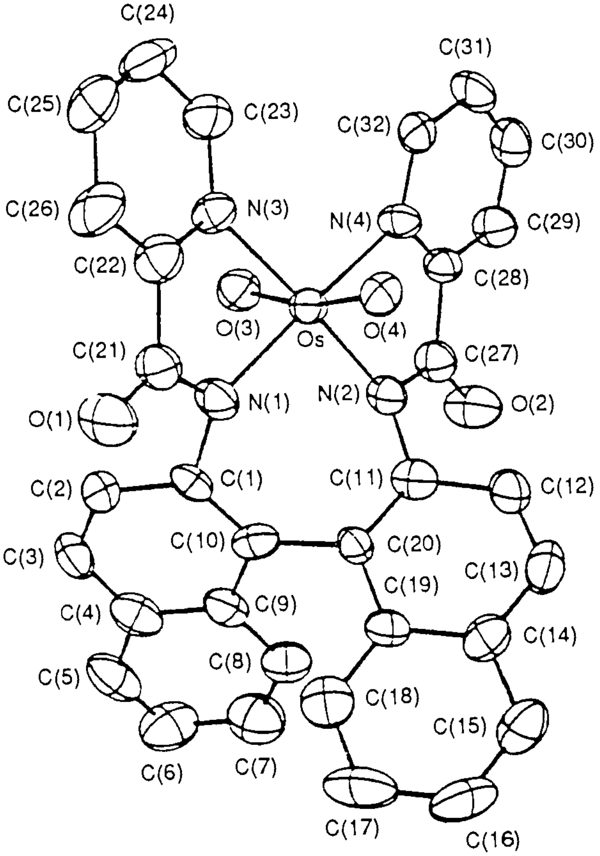


FIG. 23. ORTEP plot of the *R* form of *trans*-dioxoosmium(VI) of the binaphthyl bis(amide) ligand. From Ref. (*227*).

are unreactive and undergo irreversible electrochemical oxidation and reduction in acetonitrile.

With tetraanionic ligands, Collins and co-workers prepared the complexes $K_2[Os(\eta^4\text{-CHBA-Et})(O)_2]$ and $K_2[Os(\eta^4\text{-CHBA-DCB})(O)_2]$ from $K_2[Os(OH)_4(O)_2]$ [$\nu_{as}(OsO_2) = 820\ \text{cm}^{-1}$, $\nu_{as}(Os^{18}O_2) = 782\ \text{cm}^{-1}$] (*230*). In the presence of pyridine, these complexes reacted with PPh_3 to give bis(pyridine)osmium(IV) derivatives.

Osmyl complexes of phthalocyanine have been claimed. Reaction of OsO_4 and 1,2-dicyanobenzene at 180°C gives the dark blue $OsO_2\cdot Pc\{C_6H_4(CN)_2\}$, which is paramagnetic ($\mu_{eff} = 1.4$ BM at 20°C); so this could well be an osmium(IV) or even an osmium(III) species (*231*). Another osmyl species claimed is $OsO_2\cdot Pc\cdot 3PhNH_2$, made from

$OsO_2 \cdot Pc\{C_6H_4(CN)_2\}$ and aniline (*231*). However, no magnetic properties have been reported.

Osmyl complexes of other group V ligands are also known. The species originally thought to be $OsOCl_3(PPh_3)_2$ is now known to be mixtures containing $OsO_2Cl_2(PPh_3)_2$ [$\nu_{as}(OsO_2)$ 840 cm^{-1}] and *trans*-[$OsCl_4(PPh_3)_2$] (*232*). Similar results have also been found for $OsOBr_3(PPh_3)_2$. Both [$Os(O)_2Cl_2(PPh_3)_2$] and [$Os(O)_2Br_2(PPh_3)_2$] could be made in a pure state by reaction of OsO_4 in HCl or HBr with ethanol, and a number of $OsO_2Cl_2(PR_3)_2$ species (PR_3 = $PMePh_2$, $PEtPh_2$, PEt_2Ph) have also been made (*233*). Similar reactions with diphosphines, diarsines, and diamines also gave OsO_2X_2(L-L), where L-L is the chelating bidentate ligand (*234*).

d. Group VI Ligands. The trans-$NaK_5[Ru(O)_2(HIO_6)_2]$ complex has been prepared from $RuCl_3 \cdot nH_2O$ and IO_4^- (*235*). The X-ray crystal structure shows this to have a ruthenyl structure with coordinated $(HIO_6)^{4-}$ ligands and with Ru=O distances of 1.732(8) Å (*235*). The complex functions as an overall six-electron oxidant, oxidizing primary alcohols to carboxylic acids and secondary alcohols to ketones. It also attacks double bonds. The *trans*-$[Ru(O)_2(H_2TeO_6)_2]^{6-}$, which was prepared similarly, functions as a two-electron oxidant without the tellurato ligand functioning as an oxidizing moiety as in the iodolato analog (*235*). Reaction of RuO_4 with Ph_4PCl in glacial acetic acid gave $[Ph_4P][Ru(O)_2(CH_3COO)Cl_2] \cdot 2CH_3COOH$ (*236*). The X-ray crystal structure of the complex anion revealed a bidentate acetate and trans-chloro and *cis*-dioxo ligands. The measured Ru=O distances and O=Ru=O angle are 1.64–1.71 Å and 120.2(6)°, respectively. *trans*-Dioxoruthenium(VI) complexes containing bidentate cysteinate-*S,O* or 3-mercapto-propionate-*S,O* ligands have recently been prepared by the reaction of $Ru(O)_2(OH)_2(py)_2$ or $Ru(O)_2Cl_2(bpy)$ with *N*-acetylcysteine, *N*-formylcysteine, or 3-mercaptopropionic acid (*237*). Assignment of the *trans*-configuration came from IR spectral data, which revealed a single and intense $\nu_{as}(RuO_2)$ stretch at 800–835 cm^{-1} for these complexes.

Many osmyl complexes with group VI ligands have been reported. The purple diamagnetic potassium osmate $K_2[Os(OH)_4(O)_2]$ is the best known and is a useful starting material for the preparation of other osmyl or osmium complexes. It is best prepared from the reaction of OsO_4 with excess KOH. The X-ray crystal structure of $K_2[Os(OH)_4(O)_2]$ shows that the complex has the trans-dioxo unit, with a *d*(Os=O) of 1.77 Å and a O=Os=O angle of 180° (*238, 239*). The acid dissociation constants of "$H_2[OsO_2(OH)_4]$" have been determined.

A closely related species is the olive-green $K_2[OsO_2(OMe)_4]$, made from KOH and OsO_4 in methanol (*185*). Treatment of $[Ph_4P]_2[OsO_2Cl_4]$ with four equivalents of sodium trimethylsiloxide in dichloromethane produced $[PPh_4]_2[Os(OSiMe_3)_4(O)_2]$ in good yield (*177*). The blue $K[Os(O)_2(OAc)_3]\cdot 2AcOH$ can be prepared from $K_2[Os(O)_2(OMe)_4]$ and acetic acid, the structure of which has been established by X-ray crystallography (*240*). A bent osmyl unit (O—Os—O angle = 125.2(3)°), with d(Os=O) = 1.711 Å is *trans* to a chelating acetato ligand, the octahedral coordination being completed by two monodentate acetato ligands. Reaction of $K_2[Os(OH)_4(O)_2]$ with $NaIO_4$ and H_6TeO_6 in the presence of NaOH gave $Na_2[Os(O)_2\{IO_5(OH)\}_2]\cdot 18H_2O$ and $Na_6[Os(O)_2\{TeO_4(OH)_2\}_2]\cdot 8H_2O$, respectively. These two complexes were characterized by ^{17}O NMR spectroscopy (*241*).

The oxalato complex $[Os(O)_2(ox)_2]^{2-}$ has long been known. It is prepared by treating OsO_4 with oxalic acid and the appropriate cation. Recent electronic spectral studies on the tetrabutylammonium salt of $[Os(O)_2(ox)_2]^{2-}$ and $[Os(O)_2(malonate)_2]^{2-}$ show vibrational fine structure, similar to those found in other osmyl complexes (*242*). The salts of $M_2^I[Os(O)_2(salicylate)_2]$ have also been reported (M = Na. K, NH_4, Rb, Cs) (*185*). The ion "$[OsO_3(ox)_2]^{2-}$" may be better formulated as $[Os_2O_6ox_4]^{4-}$, rather than as the previously suggested $[Os(O)_2(OH)_2ox]^{2-}$. An $[Os(O)_2(OH)_2(SO_4)_2]$ species is said to be present in solutions of OsO_4 in H_2SO_4 (*243*). On the other hand, the osmyl complex $Na_6[Os(O)_2(SO_3)_4]\cdot 5H_2O$ made from OsO_4 and sodium sulfite in alkali is well established and has long been known [$\nu_{as}(OsO_2)$ 842 cm^{-1}]. Raman and IR spectra suggest that the sulfite is S- rather than O-bonded (*244*). Complexes of $[Os(O)_2[SC(NH_2)_2]_2]SO_4$ (*245*) and dithiocarbamato ligands (*246*) have been claimed. Osmyl complexes with thiosemicarbazides are made from the ligand and OsO_4 (*247, 248*). The osmyl thioether complexes $Os(O)_2X_2(SR)_2$ [SR_2 = SMe_2, $MeS(CH_2)_2SMe$, o-$C_6H_4(SMe)_2$, *o*-$C_6H_4(PPh_2)(SMe)$; X = Cl, Br] have recently been reported, made by reaction of the ligand with OsO_4 in concentrated HX. The seleno complexes $MeSe(CH_2)_2SeMe$ were also prepared (*249*).

A large number of osmium(VI) complexes containing the cyclic system OsOCCO [$Os(O_2R)$] are known, generally made by reaction of OsO_4 with an alkene R. Upon hydrolysis, these species gave *cis*-diols in high yields. Subsequent works showed them to be dimers, $Os_2O_4(O_2R)_2$. The complex $Os_2O_4(O_2C_2Me_4)_2$, obtained from tetramethylethylene, was established by X-ray diffraction to have an anti-structure, the osmium having a square-based pyramidal coordination [d(Os=O) = 1.675(7) Å, d(Os—O(bridge) = 1.922 Å, Os—O—Os (bridging) angle = 103.9(4)°] (*250, 251*). The bridging Os_2O_2 ring is planar. The mean O(terminal)—Os—O(based) angle is 111.1°, a distortion comparable to that found in $[Os^{VI}NX_4]^-$ species. The "diesters" of osmium(VI), $OsO(O_2R)_2$, are prepared by reaction of *cis*-diol $R(OH)_2$ with trans-$K_2[Os(O)_2(OMe)_4]$ or $K[OsO_2(OAc)_3]$, the resulting $K_2[Os(O)_2(O_2R)_2]$ then being acidified (*185*). In a few cases diesters can be obtained directly from an alkene R and OsO_4 or by prolonged reaction of a diol $R(OH)_2$ with OsO_4 (*252*). $[Os(O)(O_2C_2H_4)_2]$ derived from ethylene glycol has been shown to have a square-based pyramidal structure by X-ray crystallography (*253*). The coordination about the osmium is very similar to that found for the monoesters. The Os=O distance is 1.670(12) Å and the mean O(terminal)—Os—O(ester) angle is 110.1°. Similar distances and angles have also been observed in $Os(O)(O_2C_2Me_4)_2$ [d(Os=O) = 1.62 Å] (*254*).

There are a few examples of $K_2[Os(O)_2(O_2R)_2]$, made by reaction of diols $R(OH)_2$ with *trans*-$K_2[Os(O)_2(OMe)_4]$ or $K[Os(O)_2(OAc)_3]$. No structural data are available but the IR and Raman spectra of $K_2[Os(O)_2(O_2C_2H_4)_2]$ are consistent with an osmyl structure [$\nu_{as}(OsO_2)$ 803 cm^{-1}; $\nu_2(OsO_2)$ 859 cm^{-1}] (*182*).

Complexes of the form $Os(O)_2(O_2R)(R—py)_2$ and $Os(O)_2(O_2R)(L\text{-}L)$ are also known (L-L = phen, bpy, TMEA). A detailed review on these complexes has appeared (*185*) and will not be described here.

Catecholato complexes of the type trans-$[Os(O)_2(Rcat)_2]^{2-}$ (Rcat = catechol, 4-methylcatechol, 4-*tert*-butylcatechol, 4-nitrocatechol) are made from OsO_4 and the catechol in alkali or from the catechol and trans-$K_2[Os(O)_2(OH)_4]$. The pyridine complexes *trans*-$[Os(O)_2(Rcat)(py)_2]$ were obtained from OsO_4, pyridine, and the catechol (Rcat = cat, 4-Me-cat) [$\nu_{as}(OsO_2)$, ~820 cm^{-1}; $\nu_s(OsO_2)$, ~860 cm^{-1}] (*255*).

An unusual tetrahedral osmyl thiosulfato complex, $[Os(O)_2(S_2O_3)_2]^{2-}$, was recently prepared by reaction of OsO_4 in water with $Na_2S_2O_3$. The X-ray crystal structure revealed a *cis*-dioxo structure with O=Os=O angle and Os=O distances of 127.2(2)° and 1.692(3) Å, respectively (*256*). In CH_2Cl_2, a reversible Os(VI/V) couple at −1.10 V vs $Cp_2Fe^{+/0}$ and an irreversible oxidative wave were observed.

2. *Nitrido Complexes*

Treatment of ice-cold HX solutions of *trans*-$[Ru(O)_2X_4]^{2-}$ with sodium azide and CsX gave the brown $Cs_2[RuNX_5]$ (X = Cl, Br). With larger cations (Ph_4As^+, Bu_4N^+), the pink $[RuNX_4]^-$ was isolated (*87*). The X-ray crystal structure of $[RuNCl_4]^-$ has been determined. The Ru^{VI} is in a square-pyramidal environment with d(Ru≡N) = 1.570 Å

(*257*). Addition of L (L = py, py-*N*-oxide, isoquinoline, DMSO) or L′ (L′ = hexamethylenetetramine, pz, or dioxane) to $[RuNCl_4]^-$ gives adducts $[RuNCl_4(L)]^-$ and $\{[RuNCl_4]_2L'\}^{2-}$ (*258*).

The osmium analog $[OsNCl_5]^{2-}$ has been known for many years. It is prepared by treating $K[OsO_3N]$ with HCl (*87, 259*). Similarly, reaction of $[OsO_3N]^-$ with HBr gives $[OsNBr_5]^{2-}$, isolated as the rubidium and cesium salts (*87*). The nitrido ligand has been shown to exert a *trans* weakening influence. The *trans* halide atoms in $[OsNX_5]^{2-}$ are easily replaced by water to give *trans*-$[OsNCl_4(H_2O)]^-$.

Reaction of $[OsNX_5]^{2-}$ with $(Ph_4As)X$ (X = Cl, Br) (*87*) or $[OsO_3N]^-$ with HI and $(Ph_4As)^+$ (X = I) (*258*) gave $[OsNX_4]^-$. X-ray structures have been reported for $K_2[OsNCl_5]$ (*260*), *trans*-$K[OsNCl_4(H_2O)]$ (*261*), $K[OsNBr_4(H_2O)]$ (*261*), and $(Ph_4As)[OsNX_4]$ (X = Cl, Br, I) (*262–266*). The X-ray crystal structure of $K_2[OsNCl_5]$ shows the anion to be severely distorted with an apparently large *trans* weakening effect produced by the nitrido ligand [$d(Os{\equiv}N)$ = 1.614(13), Os—Cl(*trans*) = 2.605(4), mean Os—Cl(*cis*) = 2.361(4) Å, N—Os—Cl(*cis*) angle = 96.5(5)°] (*260*). The abnormal length of the *trans*Os—Cl bond was also attributed to nonbonding steric interaction leading to N···Cl(*cis*) and Cl···(*cis–cis*) distances of ~3.06 and 3.33 Å, respectively (*260*) ($\nu_{Os{\equiv}N}$, 1084 cm^{-1}) (*87*). In *trans*-$K[OsNCl_4(H_2O)]$ the Os≡N distance is 1.74(7) Å and Os—O distance is 2.50(3) Å (*261*). The abnormally long Os—O distance indicates that a *trans* weakening effect is apparently operative. Similarly, in *trans*-$K[OsNBr_4(H_2O)]$, the Os≡N and Os—O distances are 1.67(5) and 2.42(3) Å, respectively. The X-ray crystal structures of $Ph_4As[OsNX_4]$ (X = Cl, Br, I) have also been determined (*262–266*). All of them have a distorted square-based pyramidal structure in which the four halo ligands lie well below the osmium atom, to such an extent that the X···X distances approach the van der Waals interaction distances. It has been suggested that steric N···X repulsion is not the main cause of the distortion since the N···X and X···X distances are virtually identical despite the differences in size between N and X. An electronic repulsion effect where the $2p_x$ and $2p_y$ π electrons on the nitrido ligand are drawn toward the electronegative osmium center with concomitant repulsion interactions with the lone pairs on the halo ligands is thought to be operative (*262, 263, 265*). The reactivities of $[OsNX_4]^-$ in acetone solution have been studied in detail (*258, 267, 268*).

Ru(VI) and Os(VI) nitrido complexes of cysteine (2−) and related ligands have recently been prepared by the reactions of $[Ru(N)(CH_2SiMe_3)_4]^-$, $[Ru(N)(OSiMe_3)_4]^-$, and $[Os(N)Cl_4]^-$ with *N*-acetyl-L-cysteine, 3-mercaptoproprionic acid, and 3-mercaptopropionamide (*269*).

Similar reactions of $[Os(N)(CH_2SiMe_3)_2Cl_2]^-$ with SCN^-, 1,2-ethanedithiol, and 2-pyridinethiol also gave $[Os(N)(CH_2SiMe_3)_2(SCN)_2]^-$, $[Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]^-$, and *cis*-$[Os(N)(CH_2SiMe_3)_2(SC_5H_4N)]_2$, respectively (*270*). The X-ray crystal structures of $[Os(N)(O_2CCH_2CH_2S)_2]^-$ and $[Ru(N)(NHCOCH_2CH_2S)_2]^-$ have been determined: $d(Os{\equiv}N)$ = 1.608(7) (*271*) and $d(Ru{\equiv}N)$ = 1.595(8) Å (*269*). The X-ray crystal structure of $[Os(N)(CH_2SiMe_3)_2(SC_5H_4N)]_2$ revealed a dimer with each pyridine-2-thiolate unit chelating through sulfur and nitrogen to one metal center and bridging both metals through sulfur. The measured $Os{\equiv}N$ distances are 1.622(1) and 1.64(1) Å (*270*).

The interaction of the $[Ph_4P]^+$ salts of $[Ru(O)_2Cl_3]^-$, $[Ru(O)_2Cl_4]^{2-}$, and $[Os(O)_2Cl_4]^{2-}$ with excess *tert*-butyl isocyanate in acetonitrile forms the salts of the anions $[MN\{Bu^tNC(O)NBu^t\}Cl_2]^-$ (M = Ru or Os) (*271*). X-ray diffraction studies have shown the anions to have distorted square-pyramidal geometry with the nitrido groups in axial position [$d(Os{\equiv}N)$ = 1.629(7), $d(Ru{\equiv}N)$ = 1.588(6) Å].

Treatment of $[OsNX_4]^-$ or $[RuNCl_4]^-$ with $AsPh_3$ or $SbPh_3$(L) in methanol yields $[MNX_3L_2]$ as orange or brown solids, which are diamagnetic and exhibit $\nu(M{\equiv}N)$ at ~1030–1070 cm^{-1} (*268, 272*). Reaction of $[OsNCl_4]^-$ and PPh_3 involves a nucleophilic attack on the $Os{\equiv}N$ unit to give a paramagnetic phosphine-imidate $[Os(NPPh_3)Cl_3(PPh_3)_2]$. Similar reactions of $[M(N)Cl_3(AsPh_3)_2]$ with PR_3 (PR_3 = PPh_3, PPh_2Et, $PPhEt_2$, PEt_3, or PPh_2Me) also gave $[N(NPR_3)Cl_3(PPh_3)_2]$ (*268*). The X-ray crystal structure of $[Ru(NPPhEt_2)Cl_3(PPhEt_2)_2]$ has been determined (*273*). However, $[RuNCl_4]^-$ was reduced by PPh_3 to $[Ru^{III}Cl_4(PPh_3)_2]^-$ (*268, 272*). More basic PR_3 also reduces the osmium nitrido complexes. The $[OsNCl_4]^-$ ion will abstract sulfur from thiocyanate to give $[Os(NS)(NCS)_5]^{2-}$ (*258*). The complexes $[OsNL_2Cl_3]$ (L = PMe_2Ph, $AsPh_3$, $\frac{1}{2}$bpy, $\frac{1}{2}$phen, py) have also been shown to abstract sulfur from S_2 in a similar fashion to give the thionitrosyls $[Os(NS)L_2Cl_3]$ (*267*). A recent report showed that the $[OsNCl_4]^-$ can be alkylated to $[OsNR_nCl_{4-n}]^-$ with MgR_2, RMgX, or AlR_3 (n = 2 or 4, R = CH_2CMe_3, CH_2CH_2Ph; n = 4, R = Me) (*266*).

Treatment of $K[OsO_3N]$ with HCN produces $K[OsN(CN)_4(H_2O)]$ (*274*). A similar reaction with HF and with oxalic acid produces $K[OsNF_2(H_2O)(OH)_2]$ and a mixture of $K[OsN_2(C_2O_4)_2(H_2O)]$ and $K[OsN(C_2O_4)(OH)_2(H_2O)]$, respectively (*274*). Treatment of $[Ph_4As][Os(N)Cl_4]$ with a slight excess of NaCN in THF/MeOH gave *trans*-$[Os^{VI}(N)(CN)_4(OH)]^{2-}$, isolated as a yellow crystalline solid (μ_{eff} = 0, Λ_M = 284 Ω^{-1} cm^2 mol^{-1}, $\nu_{Os{\equiv}N}$, 1050 cm^{-1}). Recrystallization in methanol and in the presence of NaCN afforded $[Ph_4As]_2[Os^{VI}(CN)_5N]$, its structure being established by X-ray crystallography [$d(\mathrm{Os{\equiv}N}) = 1.647(7)$ Å; $d(\mathrm{Os{-}C}(\mathit{trans})) = 2.353(8)$ Å] (*275*). An $[\mathrm{Os(NH_3)_4(N)}]X_3$ (X = Cl, CF_3SO_3) complex has also been made from the oxidation of $[\mathrm{Os(NH_3)_5Cl}]Cl_2$ with excess of Ce(IV) in water at room temperature, followed by precipitation upon addition of 6 *M* HCl (*276*). Metathesis of the Cl^- salt in neat CF_3SO_3H followed by addition of diethyl ether gave the $CF_3SO_3^-$ salt ($\nu_{\mathrm{Os{\equiv}N}}$, 1090 cm^{-1}). The $[\mathrm{Ru(NH_3)_4(N)}]Cl_3$ complex was similarly prepared by Ce(IV) oxidation of $[\mathrm{Ru(NH_3)_5Cl}]Cl_2$ (*277*). This complex is characterized by IR spectroscopy ($\nu_{\mathrm{Ru{\equiv}N}}$, 1060 cm^{-1}) and easily reacts with water to give $[\mathrm{Ru(NH_3)_4(NO)(OH)}]^{2+}$. A *trans*-$[\mathrm{Os^{VI}(trpy)Cl_2(N)}]Cl$ complex has been prepared by the reaction of $[\mathrm{Os(N)Cl_4}]^{2-}$ with trpy in acetone or acetonitrile, and its crystal structure determined (*278*). The terpyridine ligand adopts a meridional configuration and is coplanar with the Os≡N unit. The measured Os≡N distance is 1.663(5) Å (*278*). This complex could be reduced reversibly in aqueous solution to give the corresponding ammine complex of Os^{II}, $[\mathrm{Os^{II}(trpy)Cl_2(NH_3)}]$, via the intermediate oxidation states, Os^V, Os^{IV}, and Os^{III}. Nitrogen atom transfer to PPh_3 and other phosphines has also been observed, giving a paramagnetic phosphoraniminato complex of Os^{IV}, *trans*-$[\mathrm{Os(trpy)Cl_2(NPPh_3)}]PF_6$ ($\mu_{\mathrm{eff}} = 1.8\,\mu_B$), characterized by X-ray crystallography. The reaction was first order in both PPh_3 and Os(VI) with $k(\mathrm{MeCN}, 25°C) = 1.36 \pm 0.08 \times 10^4\,M^{-1}\,s^{-1}$ (*279*). Reactions of $[\mathrm{Os(N)Cl_4}]^-$ with mono- or polypyridyl ligands in nonaqueous solvents have been studied. The structure of $(^n\mathrm{Bu_4N})_2[(\mathrm{OsNCl_4})_2(\mathrm{pyz})]$ has been shown by X-ray crystallography to be binuclear with two $\mathrm{Os(N)Cl_4}$ units bridged by the pyrazine ligand. The measured Os≡N distances are 1.630(7) Å (*280*).

Osmium(VI) nitrido porphyrin complexes *trans*-[Os(OEP)NX] (X = F, ClO_4, OMe) are made from $[\mathrm{Os(OEP)(O)_2}]$ and hydrazine hydrate with HF, $HClO_4$, or MeOH (*223*).

The first cyclopentadienyl nitrido complexes of a transition metal were prepared by the reactions between $[\mathrm{NBu_4}^n][\mathrm{Os(N)Cl_2(CH_2SiMe_3)_2}]$ and either NaC_5H_5 or LiC_5Me_5. The complexes $(\eta^5\text{-}C_5H_5)\mathrm{Os(N)(CH_2SiMe_3)_2}$ and $(\eta^5\text{-}C_5Me_5)\mathrm{Os(N)(CH_2SiMe_3)_2}$ were characterized by spectroscopic means (*281*). The silver-bridged complex $\{[(\eta^5\text{-}C_5H_5)\mathrm{Os(CH_2SiMe_3)_2}]_2(\mu\text{-NAgN})\}BF_4$ was characterized by X-ray crystallography: $d(\mathrm{Os{\equiv}N}) = 1.60(1)$ Å.

An osmium(VI) nitrido complex with tetraanionic chelating amide ligand was prepared by the reaction of $[\mathrm{Os}(\eta^4\text{-HBA-B})(\mathrm{PPh_3})_2]$ with phenyl azide in benzene at room temperature. The X-ray structure of $[\mathrm{Os^{VI}(N)}(\eta^4\text{-HBA-B})]^-$ revealed a square-pyramidal structure with a measured Os≡N distance of 1.64(1) Å (*282*).

Five-coordinate complexes $(NBu_4{}^n)[Os(N)(L)_4]$ have been prepared (L = CH_2SiMe_3, $OSiMe_3$, Me) (*266*). The $[OsN(CH_2SiMe_3)_4]^-$ show a $\nu(Os{\equiv}N)$ stretch at 1110 cm^{-1}, which is shifted to 1073 cm^{-1} in the ^{15}N-labeled compound (*266*). This compares well with $\nu(Os{\equiv}N)$ of 1118 and 1111 cm^{-1} for the respective $[OsN(OSiMe_3)_4]$ and $[Os(^{15}N)(OCH_3)_4]$ complexes. Electrochemical studies on $[Os(N)(CH_2SiMe_3)_4]^-$ show a quasi-reversible oxidation wave in methylene chloride (0.1 *M* NBu_4BF_4) but no reversible reduction wave has been observed (*283*). The potential for the $Os^{VI/VII}$ couple has been compared with the isoelectronic oxo and methylimido complexes (*283*). The anionic nitrido species is found to be significantly more electron rich and easier to oxidize than either the oxo or the methylimido complexes. The oxidation potential of the osmium metal has been correlated with the number of chloride ligands in the series of complexes $(NBu_4)[Os(N)Cl_{4-n}(CH_2SiMe_3)_n]$ (n = 0, 2, 4). The oxidation potentials decrease from 2.12 V for $[OsNCl_4]^-$ to 1.05 V for $[Os(N)Cl_2(CH_2SiMe_3)_2]^-$ to 0.64 V vs Ag/AgCl for $[Os(N)(CH_2SiMe_3)_4]^-$. The X-ray crystal structure of $[Os(N)(CH_2SiMe_3)_4]^-$ has been determined ($d(Os{\equiv}N)$ = 1.631(8) Å) (*284*). The reactivity has been studied and compared with the oxo and methylimido species (*283*). The complex $[Os(N)(CH_2SiMe_3)_4]^-$ is found to form 1:1 adducts with Lewis acids. It alkylates at nitrogen with organic electrophiles and reacts with mineral acids by cleavage of one or two of the metal–carbon bonds. The $[OsN(CH_2SiMe_3)_4]^-$ complex has the highest reactivity toward electrophilic attack compared to the oxo and methylimido analogs.

Similarly, the ruthenium(VI) alkyl complexes $[Ru(N)(Me)_4]^-$ and $[Ru(N)(CH_2SiMe_3)_4]^-$ have been prepared by the alkylation of $[Ru(N)(OSiMe_3)_4]^-$ with $AlMe_3$ or with $Mg(CH_2SiMe_3)_2$, respectively (*285*). The structure of $[NBu_4][Ru(N)(Me)_4]$ was determined by single-crystal X-ray crystallography (*286*). It is found to be square pyramidal, with the alkyl groups bent down below the plane of the metal, similar to the distortions observed in $[Ru(N)Cl_4]^-$ (*257*) and $[Os(N)Cl_4]^-$ (*263*), which have been ascribed to electronic repulsion between metal–nitrogen π-bonding electrons, located primarily on the central metal, and the σ-bonding electrons to the chloride ligands. The greater distortion in the methyl complex has been suggested to arise from the better electron-donating power of the methyl groups compared with the chlorides (*286*). The average N—Ru—C angle of 110.4° is comparable to the N—Os—C angle in $[NBu_4][Os(N)(CH_2SiMe_3)_4]$ of 107.4° (*284*). The N—M—Cl angle in $[Ph_4As][Ru(N)Cl_4]$ and $[Ph_4As][Os(N)Cl_4]$ are 104.6° and 104.5°, respectively. The Ru≡N distance of 1.58(1) Å in the methyl complex compares well with that of 1.570(7) Å found for $[Ph_4As][Ru(N)Cl_4]$. Mixed alkyl-chloro complexes, $[Ru(N)R_{4-x}Cl_x]^-$ (R = CH_2

$SiMe_3$, x = 1–2; R = Me, x = 1–3), have also been prepared from the reaction of HCl(g) with the alkyl complexes (*286*). Reaction with $Au(PPh_3)Cl$ results in the formation of $[Ru(N)ClMe_3]^-$ and $Au(PPh_3)Me$ from $[Ru(N)Me_4]^-$, in a manner analogous to that of the HCl reaction (*286*). In contrast to the related osmium complexes, Lewis acid adducts of the ruthenium nitrides are thermally unstable.

The electronic absorption and emission spectroscopy of Os(VI)≡N complexes have been studied in detail. Compounds containing $[OsNX_4]^-$ (X = Cl, Br) exhibit intense red luminescence (*287*). Vibronically resolved emission spectra have been obtained at 5 K. The spectra are dominated by a progression in a high-frequency ($\approx$1120 cm^{-1}) mode that corresponds to ν(Os≡N) (IR/Raman: X = Cl, ν = 1123 cm^{-1}, X = Br, ν = 1119 cm^{-1}) (*288*) as well as a long, well-defined subprogression in a mode of lower frequency (X = Cl, ν = 151 cm^{-1}, X = Br, ν = 112 cm^{-1}). The polarized single-crystal absorption spectrum of $[Ph_4As][OsNCl_4]$ at 5 K also showed vibronic structures but these features are extremely weak, consistent with the long emission lifetime of ~20 μs at 77 K and ~500 ns at 300 K. The observation of long emission lifetimes and very weak absorptions, together with a large geometric distortion along the OsN coordinate, has supported assignment of the excited state to $B_1, B_2(^3E)$ $[(d_{xy})^1(d_{xz}, d_{yz})^1]$ (C_{4V} ground state) (*287*).

Che and co-workers have also reported on the luminescent properties of $[Os^{VI}(NH_3)_4(N)]X_3$ (X = Cl, CF_3SO_3) (*276*) and $[Os^{VI}(CN)_5(N)](Ph_4As)_2$ (*275*) (Table IX). Both complexes are emissive and have long excited-state lifetimes both in solid state and in fluid solutions at room temperature (λ_{em} $\approx$ 550 nm in MeCN). The complex $[Os(NH_3)_4(N)]X_3$ has been shown to be a powerful one-electron oxidant in its excited state, with an excited-state redox potential of ~2.1 V vs NHE. The emitting state has been suggested to be $^3[(d_{xy})^1(d_\pi{}^*)^1]$ in origin.

Coupling reactions of $[Os^{VI}$≡N] and $[Os^V$≡N] have been reported. The coupling product, $[Os_2(NH_3)_8(CH_3CN)_2(\mu\text{-}N_2)]^{5+}$, has been characterized by X-ray crystallography (Fig. 24) (*151*). The reaction $[Os^{VI}(NH_3)_4(N)]^{3+} + [Os^V(NH_3)_4(N)]^{2+} \rightarrow [Os_2(NH_3)_8(CH_3CN)_2(\mu\text{-}N_2)]^{5+}$ has been found to obey second-order kinetics with a measured rate constant of 3×10^5 M^{-1} s^{-1} in MeCN at room temperature (*151*). A similar reaction has also been reported by Ware and Taube (*280*).

The electronic absorption spectra and luminescent properties of $[Os^{VI}(OEP)(N)X]$ (X = OMe, $OClO_3$) have also been studied (*223*). The emission spectra of $[Os^{VI}(OEP)(N)X]$ and $[Os^{VI}(OEP)(O)_2]$ are similar and they have comparable double lifetimes. The phosphorescence has been assigned as derived from a triplet $T_1(\pi, \pi^*)$ level.

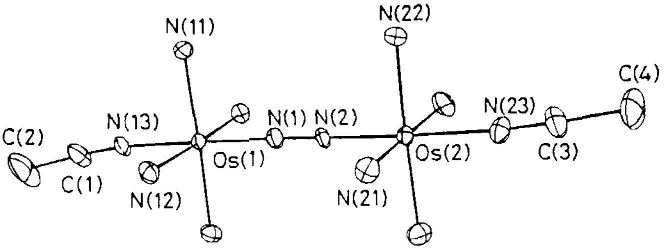


FIG. 24. ORTEP drawing of the $[Os_2(N_2)(NH_3)_8(MeCN)_2]^{5+}$ cation with atomic numbering scheme. From Ref. (*151*).

3. *Imido Complexes*

Ruthenium(VI) imido complexes are rare. Shapley reported on the reaction of $[Ru(N)R_4]^-$ with organic electrophiles such as MeI, $(Me_3O)BF_4$, $MeOSO_2CF_3$, and $Me_3SiOSO_2CF_3$. Only in the reaction of $[Ru(N)(CH_2SiMe_3)_4]$ with $Me_3SiOSO_2CF_3$ can the product $Ru(NSiMe_3)(CH_2SiMe_3)_4$ be isolated (*286*). However, no elemental analysis has been reported due to the extreme instability of the compound to air and moisture.

The isolation of the first stable oxo-*tert*-butylimido complexes of ruthenium(VI) and osmium(VI) porphyrins by oxidative deprotonation of $[M(porp)(^tBuNH_2)_2]$ has been reported (*289*). These complexes are diamagnetic and have been characterized by ^1H NMR and IR spectroscopy. The $[Ru^{VI}(porp)(O)(N^tBu)]$ complex rapidly reacts with PPh_3 in solution to give $O{=}PPh_3$, $Ph_3P{=}N^tBu$, and $[Ru(porp)(PPh_3)_2]$.

The complex $(PPh_4)[Os(NC(CCl_3)NCCl(CCl_3)Cl_5]$ may be regarded as an imido complex of osmium(VI), made by the reaction of Os_2Cl_{10} with trichloroacetonitrile and has been characterized by X-ray structural studies (*290*). The Os—N distance of 1.97(1) Å is slightly shorter than that expected for a single bond.

Recently, Schrock and co-workers synthesized the "20-electron" osmium imido complexes (*102*). Reaction of OsO_4 with 3 equivalents of ArNCO (Ar = 2,6-C_6H_3-*i*-Pr_2) for 20 h in refluxing heptane afforded the deep red-brown crystalline Os(*N*-2,6-C_6H_3-*i*-$Pr_2)_3$. An X-ray study showed that the two crystallographically distinct imido ligands are linear [Os—N(1)—C(11) = 178.0(5)°, Os—N(2)—C(21) = 180° by symmetry, *d*(Os═N) = 1.736(5), 1.738(7) Å] (Fig. 25) (*102*). The $Os(NAr)_3$ complex is stable to moist air in both the solid state and solution for days at 25°C. The Os(*N*-2,6-C_6H_3-*i*-$Pr_2)_3$ complex reacts with PMe_2Ph in pentane to give violet, crystalline $Os(NAr)_2(PMe_2Ph)_2$ and $Me_2PhP{=}NAr$ in high yield. Reaction of $Os(NAr)_3$ with Me_3NO

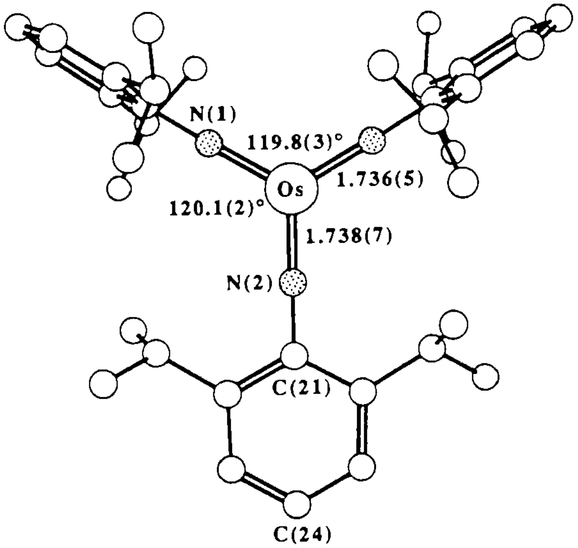


FIG. 25. A drawing of $Os(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$. From Ref. (*102*).

gave red-black crystalline $Os(O)(NAr)_3$, which readily transfers an oxygen atom to PPh_3 to give Ph_3PO and $Os(NAr)_3$. The $Os(O)(NAr)_3$ complex also reacts with norbornene, cyclopentene, and ethylene to give orange crystalline products of Os(VI) metallaimidazolidine, $[Os(ArNCH_2CH_2NAr)(O)(NAr)]$, which has been confirmed by an X-ray study (*290*).

Wilkinson and co-workers also reported on the synthesis of $Os^{VI}(NR)_3$ ($R = 2,6\text{-}Me_2C_6H_3$ or $2,6\text{-}Pr_2{}^iC_6H_3$) by reacting OsO_4 and neat NHR $(SiMe_3)$ at 100–120°C for 2–3 h (*291*). A bis(μ-*tert*-butylimido)-bis-[di(*tert*-butylimido)-osmium(VI)] complex has also been prepared by reduction of $Os(NBu^t)_4$ with triphenylphosphine or sodium amalgam in tetrahydrofuran, the X-ray crystal structure of which has been determined [d(Os···Os) = 3.120(4) Å; d(Os—N(bridge)) = 1.953(127), 1.939(12) Å; d(Os—N(terminal)) = 1.589(25) Å, 1.821(18) Å] (*291*).

An osmium(VI) oxo-imido complex, $OsO(NBu^t)(mes)_2$, has been isolated and has been discussed in Section II,C,1,b (*179*).

The first cyclopentadienyl imido complex of osmium was prepared by alkylation of the nitrogen atom in $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ by $CH_3OSO_2CF_3$ to give $[(\eta^5\text{-}C_5H_5)Os(NMe)(CH_2SiMe_3)_2](OSO_2CF_3)$, which was characterized by ^1H NMR spectroscopy [δ(NMe) = 1.5 ppm] (*281*).

D. OXIDATION STATE +VII

1. Oxo Complexes

a. Oxides, Oxoanions, and Oxohalides. Potassium perruthenate, $K[RuO_4]$, is best prepared by reduction of RuO_4 with KOH at 0°C (*159*) or by reaction of $[RuO_4]^{2-}$ with Cl_2 or NaOCl (*292*). The very dark green almost black crystals of $K[RuO_4]$ are stable in air, decomposing on heating to $K_2[RuO_4]$, RuO_2, and O_2. The X-ray crystal structure of $[RuO_4]^-$ shows a distorted tetrahedral Ru center with Ru—O = 1.79 Å and O—Ru—O angle = 106° (*293*). The IR and Raman spectra of solid $K[RuO_4]$ have been reported (*154, 155, 293*). The Mössbauer spectrum of $[RuO_4]^-$ has also been reported (*156*). There are numerous reports on the electronic absorption spectrum of perruthenate ion (λ near 390 and 320 nm); however, the assignment of these transitions has been the subject of much debate (*292, 294, 295*). Griffith and coworkers have reported the ESR spectrum of $[Pr_4{}^nN][RuO_4]$ (*296*).

In alkaline medium, $[RuO_4]^-$ is reduced to $[RuO_4]^{2-}$ with rate = $k[RuO_4{}^-]^2[OH^-]^3$ (*297*). Electron exchange between $[RuO_4]^-$ and $[RuO_4]^{2-}$ occurs with second-order kinetics rate constant $k > 3 \times 10^4$ $M^{-1}\ s^{-1}$ at 0°C; with $[MnO_4]^{2-}$ the specific rate constant for electron transfer $k = 5.7 \times 10^2\ M^{-1}\ s^{-1}$ at 20°C (*298, 299*).

$[RuO_4]^-$ oxidizes alcohols and aldehydes to ketones and carboxylic acids, and readily cleaves C=C double bonds (*159, 160, 300*). Mechanistic studies on the oxidation of organic substrates by $[RuO_4]^-$ have been reported and a concave Hammett plot has been obtained and interpreted as the involvement of free radical-like transition states that could be formed by the decomposition of organometallic intermediates (*161*). The use of $Bu_4N[RuO_4]$, prepared by the fusion of $RuCl_3$ with KNO_3 and KOH and subsequent reaction with Cl_2 and addition of Bu_4NOH, for the oxidation of alcohols to aldehydes and ketones in acetone or CH_2Cl_2 has been described (*301*).

A few of the hexa- and pentaoxo species have been prepared. The $M_5[OsO_6]$ (M = Li, Na) and $Na_3[OsO_5]$ species are formed by heating M_2O with Os in oxygen at 550°C (*162*); $K_5[OsO_6]$ and $Ba_5[OsO_6]_2$ have also been prepared (*162*). Mixed-metal $M_2{}^{II}M^I[OsO_6]$ are also known (M^{II} = Ba, Sr, Ca; M^I = Li, Na) (*163*). The $M_3{}^I[OsO_5]$ (M = Na, K) reported was tentatively suggested to be $K_6[Os_2O_{10}]$ instead on the basis of IR data (*302*).

Recently the salt $(Ph_4As)[OsO_4]$ has been reported, made by reaction of $(Ph_4As)I$ with OsO_4 in CH_2Cl_2 solution. The gray-green solid has a μ_{eff} of 1.37 μ_B, the low value being attributed to spin–orbit coupling effects. The IR spectrum shows bands at 834 and 852 cm^{-1} assigned to

$\nu_1(A_1)$ and $\nu_3(F_2)$, and the deformations ν_2 and ν_4 are at 240 cm^{-1}. A reversible OsO_4/OsO_4^- couple (E^0 = 0.1 V vs SCE) is observed in CH_2Cl_2 (*303*). The salt $[Ph_4P][OsO_4]$ is also known (*304*). The $[OsO_4]^-$, like its ruthenium counterpart, functions as an oxidant for activated alcohols, converting them to aldehydes (*305*).

$OsOF_5$ is prepared from OsO_2 and F_2, from OsO_3F_2 and F_2 (*306*), or from OsF_6/OsO_4 in a 3 : 1 ratio (*166*). The emerald green crystals are well characterized and have a distorted octahedral structure. X-ray crystal structure shows it to have a C_{4V} structure with $d(Os{=}O)$ = 1.74(3) Å and d(Os—F(*cis*)) = 1.78(3) Å, d(Os—F(*trans*)) = 1.72(3) Å (*307*). A μ_{eff} of 1.47 μ_B is obtained (*306*). Vibrational (*306*) and mass spectra (*164*) have also been measured. The yellow-green OsO_2F_3, formed from 1 : 1 mixtures of OsF_6 and OsO_4 at 150°C or OsO_3F_2 and $OsOF_4$ at 100°C, is probably polymeric. The mass spectrum indicates that monomers are present in the vapor phase; however, substantial disproportionation to OsO_3F_2 and $OsOF_4$ is also observed.

b. Group IV–VI Ligands. No Ru^{VII} nor Os^{VII} complexes with these classes of ligands have been isolated so far.

2. *Nitrido Complexes*

No Ru^{VII} nor Os^{VII} complexes of nitrido ligands have yet been isolated.

3. *Imido Complexes*

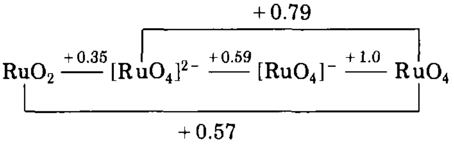
A bis(μ-*tert*-butylimido)bis[di(*tert*-butylimido)osmium(VII)]-bis(tetrafluoroborate) complex has recently been isolated, the X-ray crystal of which has been determined [d(Os···Os) = 2.68 Å, d(Os=N(terminal)) = 1.715(18), 1.710(19) Å, d(Os—N(bridge)) = 1.902(19), 1.927(20) Å] (*291*). The ^1H NMR, IR, and MS spectral data have been measured. Cyclic voltammetric experiments revealed a reversible two-electron couple at −0.07 V vs Ag/AgCl, assignable to the reduction of Os(VII) to Os(VI) (*291*).

E. OXIDATION STATE +VIII

1. *Oxo Complexes*

The most representative of these are the ruthenium tetroxide and osmium tetroxide complexes. The most widely used method of preparation of RuO_4 is by oxidation of $RuO_2{\cdot}nH_2O$ by aqueous $NaIO_4$ at 0°C followed by extraction of the RuO_4 thus generated into a suitable solvent, usually CCl_4 (*308*). The RuO_4 is toxic and highly volatile and tends to explode in the solid state (*14*). X-ray studies on solid RuO_4 only have the unit cell dimensions available; however, electron diffraction studies on RuO_4 in the vapor phase confirm a tetrahedral geometry with $d(\mathrm{Ru—O}) = 1.705$ Å (*14, 309*). Infrared and Raman spectra have been reported for RuO_4 in the solid, liquid, and gas phases. Electronic absorption, photoelectron, and MCD spectra have been measured and assigned. Studies using ^{17}O, ^{99}Ru, and ^{101}Ru NMR show that the coupling constant $J_{^{17}O-^{99}Ru}$ is 23.4 Hz in RuO_4. Mössbauer spectra for RuO_4 in the gaseous, liquid, and solid states have also been measured (*14*).

The redox chemistry of RuO_4 has been investigated. Electrochemical reduction of RuO_4 in the presence of a series of anions has been studied (*14*):



RuO_4 is an extremely powerful oxidant that was first used by Djerassi and Engle as an organic oxidant. The chemistry of RuO_4 has been reviewed (*14, 310, 311*). However, RuO_4 suffers from the disadvantage of its lack of selectivity, cleaving C=C double bonds. The most useful application of RuO_4 to organic chemistry lies in carbohydrate oxidation where secondary hydroxyl groups are converted to ketones, and the oxidation of steroid alcohols is also widely employed (*310, 311*). The reactivity of RuO_4 toward organic substrates has been reviewed (*14, 310, 311*) and compared with corresponding reactivity of OsO_4 (*312, 313*). The oxidation of alcohols, aldehydes, alkenes, alkynes, ethers, lactones, amines, amides, aromatics, sulfides, oxalic acid, and Se^{IV} by RuO_4 has been studied. The oxidation of 2-propanol in acidic medium has been studied mechanistically, proceeding via a hydride abstraction rate-determining step. At high pH, a rate-determining step involving carbonium ion formation is suggested (*314, 315*). The oxidative degradation of polychlorinated biphenyls by RuO_4 has also been investigated (*316, 317*) and oxidation of cyclic sulfites to cyclic sulfates with a catalytic RuO_4 system has recently been described by Gao and Sharpless (*318*).

Osmium tetroxide can be obtained from almost any osmium compound and a strong enough oxidant. X-ray structural studies show that solid OsO_4 contains a slightly distorted tetrahedron (O—Os—O angle of 106.7(4)° and 110.7(3)°, two Os=O distances of 1.684(7) Å, and two 1.710(7) Å) (*319*), whereas electron diffraction data on the vapor show that the vapor contains regular tetrahedral molecules with

d(Os=O) = 1.711(3) Å (*320*). Osmium tetroxide is also highly toxic and volatile with a long-term occupational exposure limit of 0.002 mg m^{-3}. Both IR and Raman spectra of OsO_4 have been reported (*185*). The four fundamental frequencies of OsO_4 have been studied in detail and the use of transitions within the OsO_4 molecule as high-precision frequency standards using CO_2 lasers has been discussed. The electronic absorption, Mössbauer, MCD, and photoelectron spectra of OsO_4 have also been measured (*185*).

Earlier polarographic data for OsO_4 have been reviewed (*321*). The reductions $Os^{VIII} \rightarrow Os^{VI}$, $Os^{VI} \rightarrow Os^{IV}$, and sometimes $Os^{IV} \rightarrow Os^{III}$ have been observed.

The chemistry of OsO_4 with alkenes, dienes, and alkynes has been reviewed (*1, 185, 322, 323*). It is used in the fine organic chemicals industry and in biological chemistry and medicine for the fixation and preservation of biological tissue. The most important process involves the *cis*-hydroxylation of alkenes by OsO_4 to vicinal glycols. Oxidations can be effected catalytically with a variety of cooxidants such as ClO_3^-, H_2O_2, TBHP, and IO_4^-. Dienes and alkynes are oxidized to glycols and α-diketones, respectively. The mechanism of alkene oxidation by OsO_4 has been subjected to detailed investigation. A probable mechanism involving a concerted (3 + 2) cycloaddition in which a direct attack by oxygen at the alkene C=C double bond leading to *cis*-addition of OsO_4 to the alkene is suggested (*322*). Other mechanisms proposed involve the formation of an osmium(VIII) four-membered oxametallacycle ring intermediate (*324*).

Recently, Hentges and Sharpless demonstrated the catalytic asymmetric osmylation of alkenes to give optically *cis*-glycols by using a chiral amine coordinated to OsO_4 (*324*). Chiral amines used for inducing chirality in the glycol include examples such as the acetates of quinidine and dihydroquinidine (*324*) with NMO as the cooxidant (*325*). A trioxoosmium(VIII) glycolato complex, $OsO_3(O_2R)L$ (L = chiral amine), is thought to be involved in the oxidative cycle (*326, 327*). The X-ray crystal structure of the 1 : 1 OsO_4—(dimethylcarbamoyl)dihydroquinidine complex has been determined to have trigonal bipyramidal geometry with an axial amine ligand (*328*). Chiral chelating diamines such as (-)-(*R,R*)-*N,N,N′,N′*-tetramethylcyclohexane-1,2-diamine) have also been employed to promote asymmetric *cis*-hydroxylations (*329, 330*).

Recently, Wallis and Kochi reported on the photochemical and thermal "osmylation" of benzene, substituted benzenes, naphthalene, and anthracene (*331, 332*). Complexes of the form $Ar \cdot OsO_4$ are formed and were studied by laser flash photolysis. In the presence of donor ligands such as pyridine, the osmium(VI) species $Os_2O_4(py)_4(O_4C_6H_6)$ and $Os_2O_4(py)_4(O_4C_{14}H_6)$ are obtained from benzene and anthracene, respectively, the X-ray crystal structures of which have been determined (*331*).

Adducts of OsO_4 with nitrogen donors are also known. They are made by reaction of OsO_4 in aqueous solution or emulsion of the amine L to give $OsO_4{\cdot}L$ [L = pyridine (*182, 333*), NH_3 (*334, 335*), pyridazine, quinuclidine (NC_7H_{13}), phthalazine, isoquinoline (*333*), and hexamethylenetetramine mandelate (*336*)] or $Os_2O_8{\cdot}L'$ (L′ = hexamethylenetetramine ($N_4C_6H_{12}$), 1,4-diazabicyclo-[2.2.2]octane, 5-methylpyrimidine, and pyrazine (*333*)]. The X-ray crystal structures of $OsO_4{\cdot}NC_7H_{13}$ and $(OsO_4)_2{\cdot}N_4C_6H_{12}$ have been obtained (d(Os—N) = 2.37 and 2.42 Å, respectively; d(Os—O) = 1.697–1.722 Å) (*337*). The symmetry of the OsO_4 unit is little disturbed. Other $OsO_4{\cdot}L$ adducts of alkaloids (L = strychnine, brucine, quinine, sparteine, cinchonine, atropine, yohimbine, cocaine, emetine) (*338–340*), blocked amino acids (L = α-*N*-benzoyl-L-histidine, α-*N*-benzoyl-DL-methionine), and imidazoles are also reported (*323*).

The Os(VIII) complexes *cis*-$[OsO_4(OH)_2]^{2-}$, $[Os_2(OH)O_8]^-$, and $[OsO_5(H_2O)]^{2-}$ are also reported (*185*). The X-ray crystal structures of *cis*-$M_2^I[OsO_4(OH)_2]$ (M^I = Li, Na) (*341, 342*) and *cis*-$M^{II}[OsO_4(OH)_2]$ (M^{II} = Ca, Sr, Ba) (*343, 344*) have been determined. The X-ray crystal structures of $M^I[Os_2(OH)O_8]$ (M^I = Rb, Cs) (*345, 346*) showed the osmium atoms to have trigonal bipyramidal structure with a bridging hydroxo ligand in the apical position. The terminal Os═O bonds lie in the range 1.62(4)–1.77(3) Å and Os—OH 2.21(2) and 2.22(2) Å (*345*). Vibrational spectra are reported for $M[OsO_4(OH)]$ and $M[OsO_4(OH)OsO_4]$ (M = Cs or Rb) and for barium and strontium osmates(VIII). The X-ray suggested that the species is in fact $Sr[OsO_3(OH)_3](OH){\cdot}2H_2O$ or $Sr[OsO_3(OH)_2(H_2O)](OH)_2{\cdot}H_2O$ (*345*).

The $M_2^I[OsO_4F_2]$ (M^I = Cs, Rb) complex has been made from excess M^IF and OsO_4. A *cis* structure is suggested from their IR and Raman spectral data (*302, 347*). Reaction of OsO_4 with $(PPh_4)Cl$ in dichloromethane gave $(Ph_4P)[OsO_4Cl]{\cdot}CH_2Cl_2$ as orange-red crystals. The X-ray crystal structure shows a trigonal bipyramidal configuration [d(Os═O) = 1.72 Å; d(Os—Cl) = 2.76(2) Å] (*348*).

The $M^I[OsO_3F_3]$ salts, made from OsO_4 and KBr, CsBr, or $AgIO_3$ in a 1 : 1 mole ratio with BrF_3 (*166*), or from MF (M = K, Rb, Cs) and OsO_3F_2 (*347*), have been reported. Infrared and Raman spectral data suggest a *fac* structure for the $Cs[OsO_3F_3]$ complex (*302*). The monomeric matrix-isolated OsO_3F_2 has been suggested to have a trigonal bipyramidal structure on the basis of vibrational spectral data (*349*).

The complex $OsO_2(OH)_2(O_2R)$ has been suggested to exist as an intermediate in the reaction of glycols $R(OH)_2$ with OsO_4 (*350*).

Oxonitrido and oxoimido complexes of Os(VIII) are included in Sections E,2 and E,3, respectively.

2. *Nitrido Complexes*

No nitrido complexes of Ru(VIII) have yet been isolated. For osmium, the only well-established osmium(VIII) nitrido species are the osmiamates, $[OsO_3N]^-$. The K^+ salt has been prepared from OsO_4 and NH_4OH in concentrated KOH solution (*351*). Free osmiamic acid can be obtained by the action of liquid ammonia on OsO_4 (*334*). Infrared studies on the free acid indicate $OsN(OH)O_2$ to be the best formulation (*274*). Osmiamates are stable in the solid state and fairly stable in aqueous solution. However, they are slowly decomposed photochemically, and on heating to 200°C give nitrogen, osmium dioxide, and potassium osmate. An X-ray radial distribution analysis on $K[OsO_3N]$ gave the Os—O and Os—N distances as 1.78(3) and 1.63(3) Å, respectively (*352*). In $Cs[OsO_3N]$, the Os—O and Os—N distances are 1.739(8) and 1.676(15) Å, respectively (*353*).

The IR and Raman spectra of $[OsO_3N]^-$ [$\nu(Os{\equiv}N)$, 1029 cm^{-1}, $\nu(Os{=}O)$, 898, 872 cm^{-1}] (*288*), $[OsO_3{}^{15}N]^-$ (*288*), and $[Os^{18}O_3N]^-$ (*354*) have been measured. The electronic absorption spectrum of $[OsO_3N]^-$ has also been reported (*355, 356*).

Other Os(VIII) nitrido complexes claimed in the literature are $[OOsN(Rbig)_2]OH{\cdot}SO_4{\cdot}nH_2O$ (Rbig = biguanide, methylbiguanide) (*357*).

3. *Imido Complexes*

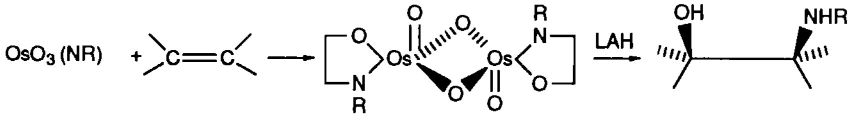
No imido complexes of Ru(VIII) have yet been reported.

Tetrakisimido complexes of $Os(NBu^t)_3(NSO_3Ar)$ (Ar = 2,4,6-trimethylphenyl, 2,4,6-triisopropylphenyl, *p*-tolyl) have been reported (*3*). However, no details have become available. Recently, Wilkinson and co-workers reported on the synthesis of the first homoleptic imido osmium(VIII) compound, $Os(NBu^t)_4$ (*291, 358*). Reaction of neat $NHBu^t(SiMe_3)$ with OsO_4 produced $Os(NBu^t)_4$ in yields varying from 25 to 40%. The IR spectrum of $Os(NBu^t)_4$ shows a $\nu(Os{=}N)$ stretch at 1238 cm^{-1} (*291*). A tetrahedral geometry has been suggested based on the IR and NMR data. The reaction of $Os(NBu^t)_4$ with PPh_3, $PMePh_2$, and PMe_3 has been investigated (*291*).

Reaction of OsO_4 with $NHBu^t(SiMe_3)$ in hexane, however, gave a mixture of $OsO_2(NBu^t)_2$ and $Os(O)(NBu^t)_3$ (*359*). The X-ray crystal structure of $OsO_2(NBu^t)_2$ shows one nearly linear [Os—N—C =

178.9(9)°] and one bent [Os—N—C = 155.1(8)°] *tert*-butylimido ligand (*359*). The Os—N bond length for the linear ligand is slightly shorter than that for the bent ligand but the difference is not significant [1.710(8) vs 1.719(8) Å]. The Os—N bond distance [average 1.713(8) Å] is exceeded by Os—O [1.744(6) Å]. This has been rationalized by the higher electronegativity of oxygen vs nitrogen, leading to the greater π-donor capability of nitrogen and hence the higher bond orders of the organoimido ligands than those of the corresponding oxo ligands.

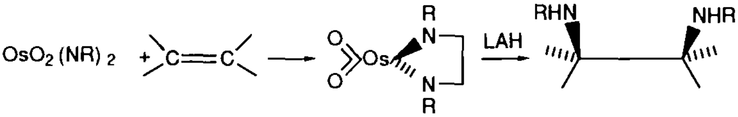
Other complexes of $OsO_3(NR)$ and $OsO_2(NR)_2$ have also been reported (R = *tert*-amyl, 1-adamantyl) (*360, 361*). The $OsO_3(NR)$ are prepared by the reaction of OsO_4 with the appropriate amine. The $OsO_3(NBu^t)$ complex has also been prepared using this method with OsO_4 reacting with *tert*-butylamine. The $OsO_2(NR)_2$ are prepared from $OsO_3(NR)$ and alkyltrialkylphosphinimine. A mixed species $OsO_2(NAm^t)(NAd)$ was prepared from $OsO_3(NAm^t)$ and *N*-1-adamantyltriphenylphosphineimine (*360*). Both $OsO_2(NR)_2$ and $OsO_3(NR)$ were found to react with monosubstituted and *trans*-disubstituted olefins to give *cis* vicinal diamines as the major products on reductive workup. In the reaction with dimethyl and diethyl fumarate, cyclic diamido complexes of osmium(VI) were isolated (*360*). The $OsO_3(NR)$ complex (R = 1-adamantyl) has been subjected to X-ray studies (*359*). The coordination around osmium is essentially tetrahedral. The organoimido ligand is nearly linear [Os—N—C = 171.4(4)°]. The Os—N bond length is very short [1.697(4) Å]. In contrast, the average Os—O bond length is longer by ~0.02 Å at 1.715(4) Å. The synthesis of $OsO_3(NOct^t)$ has also been reported (*362*). The $OsO_3(NR)$ complexes have been shown to effect an oxyamination reaction with alkenes in a stereospecific reaction (*360, 361, 363–365*):



The yield of amino alcohols has been shown to improve by addition of tertiary alkyl bulkhead amines, and catalytic cycles using chloramine-T (*364, 366, 367*) or *N*-chloro-*N*-argentocarbamates (*368*) have been devised. By the use of asymmetric inductants such as (-)-10,11-dihydroquinine with the imide, optically active amino alcohols have been produced (*369*).

Adducts of $OsO_3(NR)\cdot L$ and $[OsO_3(NR)]_2\cdot L'$ have also been isolated. The complex $OsO_3(NR)$ (R = Bu^t, 1-Ad, Oct^t) (*370, 371*) will form 1 : 1 species $OsO_3(NBu^t)\cdot L$ (L = quinuclidine, 3-quinuclidinone, 3-quinuclidinyl acetate) (*371*) and $OsO_3(NR)\cdot L$ (R = 1-Ad, Oct^t; L = quinuclidine) (*370*). The 2 : 1 species $[OsO_3(NBu^t)]_2\cdot L'$ (L' = hexamethylenetetramine, 1,4-diazabicyclo[2.2.2]octane (DABCO)] have been isolated (*371*). Similar 2 : 1 complexes with $OsO_3(NR)$ (R = Am^t, Oct^t) are also reported (*370*). The X-ray crystal structure of $[OsO_3(NOct^t)]_2\cdot$DABCO has been determined. The DABCO ligand bridges two $OsO_3(NOct^t)$ units [d(Os=N) = 1.73(1) Å; d(Os=O) = 1.71 Å (mean)] (*372*).

Reaction of $OsO_2(NR)_2$ with alkenes followed by reductive cleavage yields vicinal diamines (*360*):



A putative Os(VIII) bis(phenylimido) intermediate, which undergoes rapid insertion of an amido nitrogen into the aryl C—H bond of the second phenylimido ligand, was believed to be formed by the reaction of *trans*-[$Os(\eta^4$-HBA-B)$(PPh_3)_2$] with phenyl azide in toluene (*282*).

III. Abbreviations

OAc	acetate
ox	oxalate
py	pyridine
R-py	substituted pyridine
pyz	pyrazine
bpy	2,2'-bipyridine
R-bpy	substituted 2,2'-bipyridine
6,6'-Cl_2bpy	6,6'-dichloro-2,2'-bipyridine
4,4'$(MeO)_2$bpy	4,4'-dimethoxy-2,2'-bipyridine
5,5'-Me_2bpy	5,5'-dimethyl-2,2'-bipyridine
5,5'-$(COOH)_2$bpy	5,5'-dicarboxyl-2,2'-bipyridine
biq	2,2'-biquinoline
trpy	2,2'–6',2''-terpyridine
phen	1,10-phenanthroline
2,9-Me_2phen	2,9-dimethyl-1,10-phenanthroline
tpm	tris(1-pyrazolyl)methane
pic	picolinate anion
PnR_3	tertiary phosphine or arsine
en	ethylenediamine

TMEA	*N,N,N′,N′*-tetramethylethylenediamine
tmcn	*N,N,N′,N′*-tetramethylcyclohexanediamine
Me$_3$tacn	*N,N,N′,N′*-trimethyl-1,4,7-triazacyclononane
14TMC	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
15TMC	1,4,8,12-tetramethyl-1,4,8,12-tetraazacyclopentadecane
16TMC	1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane
CRMe$_3$	*meso*-1,2,6,10,11-pentamethyl-2,6,10-triaza[11](2,6)pyridinophane
Tet-Me$_6$	*N,N,N′,N′*-tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine
pytn	*N,N′*-dimethyl-bis(2-pyridylmethyl)propylenediamine
pyen	*N,N′*-dimethyl-bis(2-pyridylmethyl)ethylenediamine
N$_4$OH	bis(2-(2-pyridyl)ethyl)(2-hydroxy-2-(2-pyridyl)ethyl)amine
N$_2$O$_2$	1,12-dimethyl-3,4 : 9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane
BiQN	1,1′-bi-isoquinoline
isn	isonicotinamide
H$_4$CHBAEt	1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane
H$_4$CHBA-DCB	1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene
H$_4$-HBA-B	1,2-bis(2-hydroxybenzamido)benzene
Pc	phthalocyanine
salen	N,N′-bis(salicylidene)ethylenediaminato
3-*t*-Bu-saltmen	N,N′-(1,1,2,2-tetramethylethylene)bis(3-*tert*-butylsalicylideneaminato)
saloph	N,N′-bis(salicylidene)-*o*-phenylenediaminato
H$_2$bpb	1,2-bis(pyridine-2-carboxamido)benzene
Im	imidazole
2-Me-Im	2-methylimidazole
Rcat	substituted catechol
edta	*N,N,N′,N′*-ethylenediaminetetraacetate
sar	3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
Cp	cyclopentadienyl
H$_2$TMP	5,10,15,20-tetramesitylporphyrin
H$_2$OEP	octaethylporphyrin
H$_2$TPP	*meso*-tetraphenylporphyrin
H$_2$TTP	*meso*-tetra(*p*-methylphenyl)porphyrin
H$_2$TPr^{n}P	*meso*-tetrakis(*p*-*n*-propylphenyl)porphyrin
NMO	*N*-methylmorpholine *N*-oxide
L$_{OEt}$	$[CpCo\{(EtO)_2P{=}O\}_3]^-$
mes	mesityl
mCPBA	*meta*-chloroperbenzoic acid
TBHP	*tert*-butyl hydroperoxide
PhIO	iodosylbenzene

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