Transition-metal Periodato Complexes. Their Preparations and Properties as Catalytic Oxidants, and X-Ray Crystal Structure of $Na_4K[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 15H_2O$ *

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The preparations and properties as oxidants for alcohols, aldehydes and activated primary alkyl halides of $[M\{IO_5(OH)\}_2]^{5-}$ (M = Cu, Ag or Au), $[M(OH)_2\{IO_5(OH)\}_2]^{6-}$ (M = Ni, Pd or Pt), *trans*-$[MO_2\{IO_5(OH)\}_2]^{6-}$ (M = Ru or Os) and $[M_6O_{24}I]^{5-}$ (M = Mo or W) are reported. The X-ray crystal structure of $Na_4K[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 15H_2O$ shows the gold atom to be square planar with co-ordination by two bidentate $[IO_5(OH)]^{4-}$ ligands; the $[Au\{IO_5(OH)\}_2]^{5-}$ units are linked by NaO_6 octahedra to form polymeric chains which are cross-linked by potassium ions.

In an earlier paper[1] we reported the X-ray crystal structure of *trans*-$NaK_5[RuO_2\{IO_5(OH)\}_2]\cdot 8H_2O$ and the oxidation reactions of the *trans*-$[RuO_2\{IO_5(OH)\}_2]^{6-}$ ion. At the time this species was unique as a 'double oxidant' in which both the central Ru^{VI} atom and the $[IO_5(OH)]^{4-}$ ligands each function as two-electron oxidants, converting primary alcohols to carboxylic acids and secondary alcohols to ketones. Such reactions are catalytic in the presence of periodate as co-oxidant. We have now investigated other periodato complexes of transition metals in high oxidation states to establish whether these too might function as double oxidants for organic substrates. Transition-metal periodato complexes are ill-defined and rarely fully characterised[2,3] and reported methods of preparation are often unsatisfactory, so another purpose was to optimise their preparations and establish proper stoichiometries for the complexes. We also report for the first time the X-ray crystal structure of a salt containing the $[Au\{IO_5(OH)\}_2]^{5-}$ ion.

The copper,[4,5] silver[6] and gold[7] complexes are unusual in containing the metal in the trivalent oxidation state. It was suggested that they should be formulated as $[M\{IO_5(OH)\}_2]^{5-}$ (M = Cu,[5] Ag[5] or Au[7]), and this was subsequently confirmed by X-ray studies on $Na_4K[Cu\{IO_5(OH)\}_2]\cdot 12H_2O$,[8] $K_4H_4Cu(IO_6)_2(O_2)\cdot 6H_2O$[9] and $K_5[Ag\{IO_5(OH)\}_2]\cdot 8H_2O$;[10] all showed square-planar co-ordination about the metal. The nickel complex '$K[NiO_6]\cdot 1.5H_2O$' lacks characterisation[11] but $[Ni(OH)_2\{IO_5(OH)\}_2]^{6-}$ is known.[12] Sodium and potassium salts of $[M(OH)_2\{IO_5(OH)\}_2]^{6-}$ (M = Pd or Pt),[13] and the salt $Na_6[OsO_2\{IO_5(OH)\}_2]\cdot 18H_2O$[14] have been reported, and the X-ray crystal structures of *trans*-$Na_2K_4[Pt(OH)_2\{IO_5(OH)\}_2]\cdot 10H_2O$[13] and $NaK_5[RuO_2\{IO_5(OH)\}_2]\cdot 8H_2O$[1] determined. Very recently the X-ray crystal structure of $Na_7[Mn\{IO_5(OH)\}_2\{IO_4(OH)_2\}]\cdot 18H_2O$ has been reported.[15] The heteropolyoxometalate in $K_5[IMo_6O_{24}]\cdot 6H_2O$ has an Anderson-type D_{3d} structure in which an IO_6 octahedron is surrounded by six MoO_5 groups such that the IMo_6 unit is planar.[16]

Results and Discussion

Preparations.—There is a dearth of information on detailed, reliable preparative methods for most of the complexes mentioned in this paper, and all the preparations in the Experimental section are either new or contain substantial modifications of literature procedures. Salts of the new species $[Pd\{IO_5(OH)\}_2]^{6-}$ and $[IW_6O_{24}]^{5-}$ are reported, the latter being made by methods similar to those used for the preparation of $[IMo_6O_{24}]^{5-}$.[17]

X-Ray Crystal Structure of $Na_4K[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 15H_2O$.—Although the X-ray crystal structures of $Na_4K[Cu\{IO_5(OH)\}_2]\cdot 12H_2O$,[8] $K_4H_4Cu(IO_6)_2(O_2)\cdot 6H_2O$[9] and $K_5[Ag\{IO_5(OH)\}_2]\cdot 8H_2O$[10] have been reported there are no data on the structure of gold periodato complexes. We have therefore prepared the new compound $Na_4K[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 15H_2O$ and obtained its X-ray crystal structure. The yellow-green crystals were obtained by the slow evaporation of a solution of the complex with 1 mol dm^{-3} aqueous NaOH in a vacuum desiccator. Selected bond lengths and angles of the refined structure are given in Table 1, and the atomic coordinates are listed in Table 2.

The structure of the complex anion [Fig. 1(*a*)] shows that the gold, which is positioned on a crystallographic centre of symmetry, is square planar. This central gold atom is bound to two octahedral $[IO_5(OH)]^{4-}$ units. The $[Au\{IO_5(OH)\}_2]^{5-}$ anion is slightly folded [Fig. 1(*b*)] with the planes formed by I, O(1), O(3), O(4) and O(6) inclined by *ca.* 10° to the co-ordination plane of the gold atom. The Au–O(1) and Au–O(6) distances are 1.978(5) and 1.975(4) Å respectively, and the O(1)–Au–O(6) angle is 78.8(2)°. This angle is comparable with those found about copper in $Na_4K[Cu\{IO_5(OH)\}_2]\cdot 12H_2O$[8] and about silver in $K_5[Ag\{IO_5(OH)\}_2]\cdot 8H_2O$[10] (84.2 and 79.7° respectively). Each IO_6 octahedron is slightly distorted, with the angles at I in the ranges 79.1–98.9° and 169.9–175.4°, the largest distortions being for O(1)–I–O(6) [79.1(2)] and O(3)–I–O(4) [98.9(2)°]. The former satisfies the 'bite' of the ligand and is very close to that observed in $K_5[Ag\{IO_5(OH)\}_2]\cdot 8H_2O$[10] (which has a mean value of *ca.* 80°). The latter is also comparable with those found in other periodato complexes, *e.g.* *trans*-$NaK_5[RuO_2\{IO_5(OH)\}_2]\cdot 8H_2O$ (97.0°),[1] $Na_4K[Cu\{IO_5(OH)\}_2]\cdot 12H_2O$ (95.3°),[8] $K_5[Ag\{IO_5(OH)\}_2]\cdot 8H_2O$ (95.6°)[9] and *trans*-$Na_2K_4[Pt(OH)_2\{IO_5(OH)\}_2]\cdot 10H_2O$ (98.0°).[13] The bridging I–O(1) and I–O(6) distances are essentially the same at 1.972(4) and 1.968(5) Å, and the *trans* annular O(1)···O(6) and Au···I distances are 2.51(1) and 3.034(1) Å respectively. The I–O(3) and I–O(4) distances are also very similar to each other at 1.816(5) and 1.829(4) Å respectively. The axial I–O(2) and I–O(5) distances, 1.882(4)

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Bond lengths (Å) and angles (°) for $Na_4K[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 15H_2O$

Au–I	3.034(1)	Au–Na(1)	3.474(3)	K–O(7′)	2.778(5)	Na(1)–Na(2)	3.389(5)
Au–O(1)	1.978(5)	Au–O(6)	1.975(4)	Na(1)–O(2)	2.419(5)	Na(1)–O(6)	2.502(5)
I–Na(1)	3.449(3)	I–O(1)	1.972(4)	Na(1)–O(7)	2.375(6)	Na(1)–O(8)	2.370(5)
I–O(2)	1.882(4)	I–O(3)	1.816(5)	Na(1)–O(9)	2.419(5)	Na(1)–O(10)	2.397(6)
I–O(4)	1.829(4)	I–O(5)	1.855(5)	Na(2)–O(9)	2.402(7)	Na(2)–O(10)	2.530(6)
I–O(6)	1.968(5)	K–Na(1)	3.775(3)	Na(2)–O(11)	2.429(8)	Na(2)–O(12)	2.554(7)
K–O(8)	2.733(4)	K–O(10)	3.037(5)	Na(2)–O(13)	2.333(10)	Na(2)–Na(2′)	3.429(7)
K–O(1′)	2.683(4)	K–O(3′)	3.043(5)	Na(2)–O(11′)	2.382(7)		
K–O(5′)	3.093(5)	K–O(6′)	2.690(5)				
O(1)–Au–O(6)	78.8(2)	O(1)–Au–O(6′)	101.2(2)	O(10)–K–O(7′)	146.9(1)	O(1′)–K–O(7′)	99.8(1)
O(1)–Au–O(1′)	180.0	O(6)–Au–O(6′)	180.0	O(3′)–K–O(7′)	154.6(1)	O(5′)–K–O(7′)	111.3(2)
Au–O(1)–I	100.4(2)	Au–O(6)–I	100.6(2)	O(6′)–K–O(7′)	82.8(2)	O(2)–Na(1)–O(6)	65.5(2)
Au–O(6)–Na(1)	101.1(2)	O(1)–I–O(2)	88.4(2)	(02)–Na(1)–O(7)	164.6(2)	O(6)–Na(1)–O(7)	103.1(2)
O(1)–I–O(3)	90.8(2)	O(2)–I–O(3)	91.6(2)	O(2)–Na(1)–O(8)	101.2(2)	O(6)–Na(1)–O(8)	95.5(2)
O(1)–I–O(4)	170.3(2)	O(2)–I–O(4)	90.2(2)	O(7)–Na(1)–O(8)	89.8(2)	O(2)–Na(1)–O(9)	78.9(2)
O(3)–I–O(4)	98.9(2)	O(1)–I–O(5)	88.0(2)	O(6)–Na(1)–O(9)	84.2(2)	O(7)–Na(1)–O(9)	90.0(2)
O(2)–I–O(5)	175.4(2)	O(3)–I–O(5)	91.3(2)	O(8)–Na(1)–O(9)	179.7(2)	O(2)–Na(1)–O(10)	101.6(2)
O(4)–I–O(5)	92.8(2)	O(1)–I–O(6)	79.1(2)	O(6)–Na(1)–O(10)	167.1(2)	O(7)–Na(1)–O(10)	89.5(2)
O(2)–I–O(6)	87.5(2)	O(3)–I–O(6)	169.9(2)	O(8)–Na(1)–O(10)	87.5(2)	O(9)–Na(1)–O(10)	92.8(2)
O(4)–I–O(6)	91.2(2)	O(5)–I–O(6)	89.0(2)	O(9)–Na(2)–O(10)	90.0(2)	O(9)–Na(2)–O(11)	81.2(2)
I–O(6)–Na(1)	100.3(2)	I–O(2)–Na(1)	106.0(2)	O(10)–Na(2)–O(11)	93.6(2)	O(9)–Na(2)–O(12)	83.4(2)
O(8)–K–O(10)	69.5(1)	O(8)–K–O(1′)	167.7(2)	O(10)–Na(2)–O(12)	79.5(2)	O(11)–Na(2)–O(12)	163.1(3)
O(10)–K–O(1′)	111.0(1)	O(8)–K–O(3′)	124.2(1)	O(9)–Na(2)–O(13)	177.4(3)	O(10)–Na(2)–O(13)	88.1(3)
O(10)–K–O(3′)	55.4(1)	O(1′)–K–O(3′)	55.8(1)	O(11)–Na(2)–O(13)	100.6(3)	O(12)–Na(2)–O(13)	94.6(3)
O(8)–K–O(5′)	115.0(1)	O(10)–K–O(5′)	79.4(1)	O(9)–Na(2)–O(11′)	95.1(2)	O(10)–Na(2)–O(11′)	174.6(3)
O(1′)–K–O(5′)	54.3(1)	O(3′)–K–O(5′)	50.7(1)	O(11)–Na(2)–O(11′)	89.1(3)	O(12)–Na(2)–O(11′)	99.2(3)
O(8)–K–O(6′)	85.0(1)	O(10)–K–O(6′)	98.8(2)	O(13)–Na(2)–O(11′)	86.8(3)	Na(1)–O(9)–Na(2)	89.3(2)
O(1′)–K–O(6′)	106.8(2)	O(3′)–K–O(6′)	109.5(2)	Na(1)–O(10)–Na(2)	86.9(2)	Na(2)–O(11)–Na(2′)	90.9(3)
O(5′)–K–O(6′)	157.1(1)	O(8)–K–O(7′)	77.8(1)				

* Atoms denoted by primes are those produced by one of the crystallographic centres of symmetry.

Table 2 Atomic coordinates (× 10⁴) for $Na_4K[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 15H_2O$

Atom	*x*	*y*	*z*
Au	0	0	0
I	62(1)	−2 198(1)	2 026(1)
K	−4 834(2)	6 855(2)	945(1)
Na(1)	−3 522(4)	1 694(3)	1 841(2)
Na(2)	−5 949(6)	1 719(5)	4 145(3)
O(1)	1 784(6)	−719(6)	1 037(3)
O(2)	−750(6)	−1(6)	2 647(3)
O(3)	2 112(7)	−2 907(7)	2 763(3)
O(4)	−1 877(7)	−3 393(6)	2 821(3)
O(5)	856(7)	−4 240(6)	1 319(4)
O(6)	−1 828(7)	−1 160(6)	1 077(3)
O(7)	−6 459(7)	2 525(7)	1 048(4)
O(8)	−1 875(7)	3 908(6)	697(3)
O(9)	−5 204(7)	−576(7)	3 000(4)
O(10)	−4 621(8)	4 200(7)	2 838(4)
O(11)	−2 634(11)	377(10)	4 545(5)
O(12)	−9 027(8)	2 770(7)	3 245(4)
O(13)[a]	−6 725(14)	4 048(12)	5 200(6)
O(14A)[a]	−9 968(15)	4 549(15)	5 924(8)
O(14B)[a]	−11 258(18)	2 720(16)	5 306(8)
O(15A)[b]	−9 275(21)	1 389(21)	5 524(16)
O(15B)[b]	−7 695(20)	5 961(20)	4 757(14)

[a] Occupancy 50%. [b] Occupancy 25%.

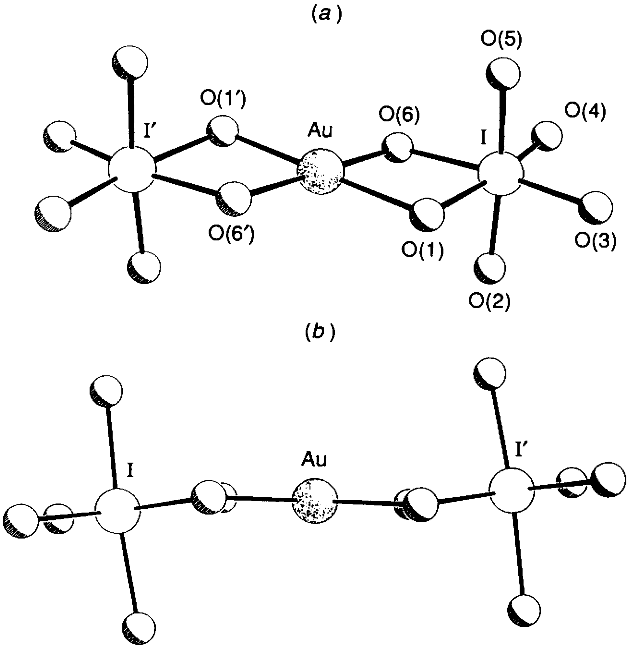

Fig. 1 Perspective (*a*) and edge-on (*b*) views of the $[Au\{IO_5(OH)\}_2]^{5-}$ anion in the crystal structure of $Na_4K[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 15H_2O$. Primed atoms are related to their parents by a centre of symmetry

and 1.855(5) Å, are very much closer to each other than those observed in $Na_4K[Cu\{IO_5(OH)\}_2]\cdot 12H_2O$,[8] $K_5[Ag\{IO_5(OH)\}_2]\cdot 8H_2O$[10] and $Na_2K_4[Pt(OH)_2\{IO_5(OH)\}_2]\cdot 10H_2O$,[13] where differences of >0.1 Å are observed between these bonds. In the absence of the location of the hydroxylic hydrogen atoms we tentatively assign the I=O to be associated with I–O(5). The equatorial atoms of the IO_6 octahedron are coplanar to within 0.012 Å (for I), the iodine atom lying 0.015 Å out of the plane of the four oxygen atoms and in the direction of O(5).

Pairs of $[Au\{IO_5(OH)\}_2]^{5-}$ anions are linked to form continuous chains by two pairs of edge-to-edge linked NaO_6 octahedra (Fig. 2) which are in turn linked edge-to-edge with the IO_6 octahedra (Fig. 3). The geometries of the sodium octahedra are listed in Table 1. The non-bonded I ··· Na(1), Na(1) ··· Na(2) and Na(2) ··· Na(2′) distances are 3.45, 3.39 and 3.43 Å respectively. The potassium ions serve to bridge

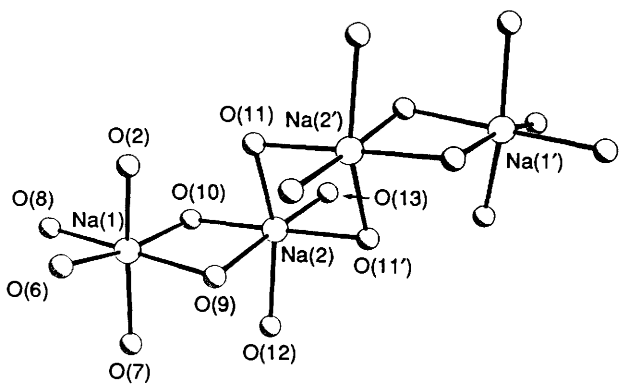

Fig. 2 Linking of pairs of NaO_6 octahedra in the crystal structure

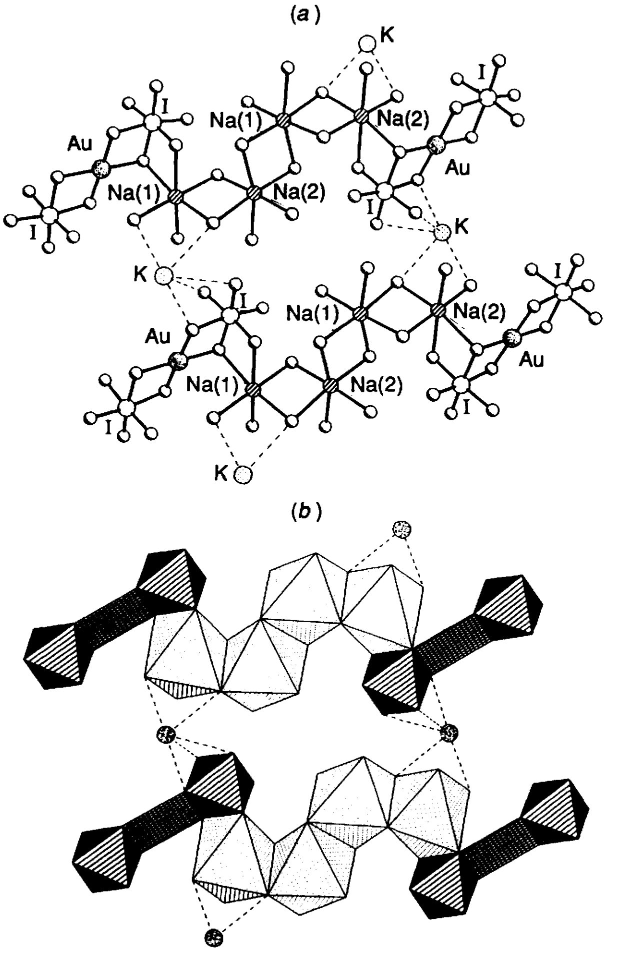

Fig. 3 (a) Part of the continuous linked chain of anions and cations in the crystal structure of $Na_4K[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 15H_2O$; (b) Edge-to-edge linking of octahedra with the cross-linking potassium atoms shown as circles

adjacent chains in two directions in the crystal, forming four short and three longer contacts (Fig. 4 and Table 1). Some of the water molecules in the lattice were found to have only partial occupancies, reflecting the ready loss of water by the crystals which are observed to decompose on standing (becoming a milky white colour). A detailed analysis of the extensive hydrogen bonding network that clearly must exist is not realistic in the absence of the location of hydrogen atom positions.

We were unable to obtain crystals suitable for X-ray structural studies for the complexes containing $[Pd\{IO_5(OH)\}_2]^{6-}$, $[M(OH)_2\{IO_5(OH)\}_2]^{6-}$ (M = Ni or Pd) or $[OsO_2\{IO_5(OH)\}_2]^{6-}$; however, X-ray powder diffraction patterns show that $Na_6[MO_2\{IO_5(OH)\}_2]\cdot 18H_2O$ (M = Ru or Os) are isomorphous and the Raman and infrared spectra are very similar[18] so it is likely that the osmium complex contains the *trans*-$[OsO_2\{IO_5(OH)\}_2]^{6-}$ ion. Furthermore, features of the Raman and infrared spectra of $Na_6[Ni(OH)_2\{IO_5(OH)\}_2]\cdot H_2O$ and $Na_6[Pd\{IO_5(OH)\}_2]\cdot 11H_2O$ (data reported in Experimental section) show similarities to those for the other periodato complexes described herein.[18] The Raman and infrared spectra of $K_5[IMo_6O_{24}]\cdot 6H_2O$ and of $K_5[IW_6O_{24}]\cdot 6H_2O$ are also very similar[18] suggesting that these too have the same structures.

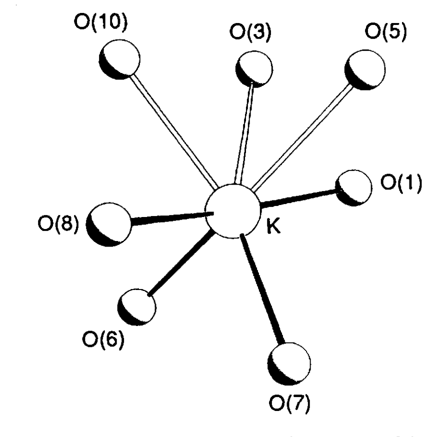

Fig. 4 Co-ordination about the potassium atom. The solid bonds correspond to short K–O distances and open lines to the longer ones

Organic Oxidations by the Complexes.—Apart from our development of *trans*-$[RuO_2\{IO_5(OH)\}_2]^{6-}$ as a viable catalyst for the oxidation of primary alcohols to carboxylic acids and secondary alcohols to ketones in the presence of periodate as co-oxidant in aqueous base[1] the only studies in the literature are of the kinetics of stoichiometric oxidation of some organic substrates by periodato complexes. Thus it has been shown that $[M\{IO_5(OH)\}_2]^{5-}$ oxidises primary and secondary alcohols (M = Cu[19,20] or Ag[21]); there are also studies on the oxidation of cyclic ketones to 2-hydroxy cyclic ketones,[22] acetophenones to phenacyl alcohols[23] and of aldehydes to ketones[24] by $[Ag\{IO_5(OH)\}_2]^{5-}$.

Our studies have concentrated on establishing whether periodato complexes are useful organic oxidants, to find the nature of the products of oxidation and to ascertain whether such oxidations can be rendered catalytic. We were also interested in establishing whether any of these complexes were 'double oxidants' in the sense that both metal and ligand might have an oxidising role.

Stoichiometric oxidations. We find that all the complexes oxidise primary alcohols and also activated primary alkyl halides to aldehydes and carboxylic acids and secondary alcohols to ketones.

Movius[19] has shown that $[Cu\{IO_5(OH)\}_2]^{5-}$ functions as a one-electron oxidant for alcohols, giving a copper(II) periodato complex; we have confirmed this by reacting known amounts of 4-methoxybenzyl alcohol and the complex and quantifying the yield of aldehyde and acid produced over a 1 h period in aqueous KOH. Similarly Rao *et al.*[21] have shown that $[Ag\{IO_5(OH)\}_2]^{5-}$ is a two-electron oxidant for alcohols; we have confirmed this and also find that $[Au\{IO_5(OH)\}_2]^{5-}$ is a two-electron oxidant for alcohols. This suggests that for $[M\{IO_5(OH)\}_2]^{5-}$ (M = Cu, Ag or Au) only the metal(III) centre acts as an oxidant, giving Cu^{II}, Ag^{I} and Au^{I} species as products (we have attempted to identify these inorganic reduction products but without success). In the case of the new complex $Na_6[Pd\{IO_5(OH)\}_2]\cdot 11H_2O$ a four-electron change occurs, and iodate (as KIO_3) can be recovered at pH 12 from the reaction mixture, indicating that here only the periodato ligands are involved in oxidation. Thus these complexes are not double oxidants. We have already reported that $[RuO_2\{IO_5(OH)\}_2]^{6-}$ is an overall six-electron oxidant involving both the metal centre and the periodato ligands;[1] we find this also to be the case for the osmium analogue, and for $[M(OH)_2\{IO_5(OH)\}_2]^{6-}$ (M = Ni or Pt).

With activated primary halides, *e.g.* 4-methoxybenzyl chloride, the situation is somewhat different. In this case $[Cu\{IO_5(OH)\}_2]^{5-}$ functions as an overall three-electron oxidant while $[M\{IO_5(OH)\}_2]^{5-}$ (M = Ag or Au) are four-electron oxidants; presumably the metal and one periodato ligand are involved, although we are unable to identify the inorganic products with certainty. The other complexes, *viz.* $[Pd\{IO_5(OH)\}_2]^{6-}$, $[M(OH)_2\{IO_5(OH)\}_2]^{6-}$ (M = Ni or Pt) and $[MO_2\{IO_5(OH)\}_2]^{6-}$ (M = Ru or Os) behave in a similar fashion with primary alcohols.

Catalytic oxidations. We tested all the complexes so far mentioned for possible catalytic activity by taking 0.01 mmol of the complex in aqueous 0.25 mol dm^{-3} KOH solution with KIO_4 (2.2 mmol) as co-oxidant with 1 mmol of substrate, the reactions being carried out for 3 h in the case of alcohols and aldehydes and 4 h in the case of alkyl halides, all at room temperature. Aldehydes or ketones were detected and quantified as 2,4-dinitrophenylhydrazine derivatives and acids isolated and weighed as such. Blank experiments were conducted under similar conditions, but in the absence of complex; in all cases only small amounts of oxidation products were found {*e.g.* less than 8% of aldehyde from 4-methoxybenzyl alcohol and less than 12% of α-tetralone [3,4-dihydro-1(2*H*)-naphthalenone] from α-tetralol (1,2,3,4-tetrahydro-1-naphthol) after 4 h}.

Under such conditions (see Table 3) $[M\{IO_5(OH)\}_2]^{5-}$ (M = Cu, Ag or Au) do not function catalytically. However, $[M(OH)_2\{IO_5(OH)\}_2]^{6-}$ (M = Ni or Pt), $[Pd\{IO_5(OH)\}_2]^{6-}$ and $[MO_2\{IO_5(OH)\}_2]^{6-}$ (M = Ru or Os) do function as quite efficient catalysts for the oxidation of alcohols, aldehydes and primary activated alkyl halides to aldehydes and/or acids, and secondary alcohols to ketones. Under phase-transfer conditions [water–1,2-dichloroethane (1:1) with Aliquat 336 (tricaprylmethylammonium chloride] the aldehydes are cleanly extracted into the non-aqueous layer. The palladium(IV) complex $[Pd(OH)_2\{IO_5(OH)\}_2]^{6-}$ only gives substantial oxidation under phase-transfer conditions: the reason for its inactivity as a catalytic oxidant in aqueous solution is not clear. We also studied the oxidation of diols [hydrobenzoin (1,2-diphenylethane-1,2-diol), *cis*- and *trans*-cyclohexane-1,2-diol, cycloheptane-1,2-diol] with these reagents; only in the case of hydrobenzoin were substantial yields of benzil and benzoic acid obtained, but periodate itself is a known reagent for cleavage of diols.[25]

Although $[OsO_2\{IO_5(OH)\}_2]^{6-}$ appears to be the most efficient complex it is almost certain that OsO_4 {or more probably *cis*-$[OsO_4(OH)_2]^{2-}$ produced[26] from OsO_4 and OH^-} is the active oxidant; it is likely that excess periodate in base would oxidise the complex to *cis*-$[OsO_4(OH)_2]^{2-}$. In agreement with this we find that solutions of OsO_4 (1×10^{-6} mol dm^{-3}) in 0.25 mol dm^{-3} aqueous KOH and $NaIO_4$ (2×10^{-3} mol dm^{-3}) will oxidise 4-methoxybenzyl alcohol and 4-methoxybenzyl chloride to the aldehyde and acid giving very similar yields and turnovers to those given in Table 3, and furthermore the electronic spectrum of $[OsO_2\{IO_5(OH)\}_2]^{6-}$ in 0.25 mol dm^{-3} KOH is close to that of OsO_4 in a similar solution of base and periodate. In addition, $[OsO_2\{IO_5(OH)\}_2]^{6-}$ (0.01 mmol) in 0.25 mol dm^{-3} aqueous KOH and periodate (1 mmol) reacts with *cis*- and *trans*-stilbene at room temperature over 2 h to give benzaldehyde (74% yield, turnover 50) suggesting that C=C bond cleavage has occurred after hydrolysis of an osmate ester, as would be expected with an OsO_4-containing reagent.

Oxidations by $[IM_6O_{24}]^{5-}$ (M = Mo *or* W). The hexadecylpyridinium salt $[C_5H_5N(CH_2)_{15}CH_3]_4K[IMo_6O_{24}]$ catalyses the oxidation of primary alcohols to aldehydes and secondary alcohols to ketones by hydrogen peroxide under two-phase (1,2-dichloroethane–water) conditions at 50 °C; with cinnamyl alcohol there was no evidence of products arising from cleavage of the double bond (Table 4). Similar turnovers for the oxidation of alcohols to carbonyl compounds in 1,2-dichloroethane–water were obtained by using $K_5[IMo_6O_{24}]$ and Aliquat 336; $[IW_6O_{24}]^{5-}$ gave similar results to those of $[IMo_6O_{24}]^{5-}$. Under two-phase reflux conditions and H_2O_2 at temperatures up to 80 °C $[C_5H_5N(CH_2)_{15}CH_3]_4K[IMo_6O_{24}]$ oxidation of oct-2-ene at 80 °C gave only a mixture of 80% unreacted alkene, 10% of 1,2-epoxyoctane, 10% of octan-1-al, and similar low, mixed yields of epoxide and aldehyde were obtained for hex-1-ene and dec-1-ene. Activated alkyl halides such as *p*-methoxybenzyl chloride and benzyl bromide are only stoichiometrically oxidised to aldehydes by H_2O_2 in the presence of $[C_5H_5N(CH_2)_{15}CH_3]_4K[IMo_6O_{24}]$ under biphasic conditions, although use of the tetrahexylammonium salt $[N(C_6H_{13})_4]_3K_2[IMo_6O_{24}]$ in CH_2Cl_2 with $[NBu_4]IO_4$ as co-oxidant increased the turnover to 10.

Experimental

Physical Measurements and Analyses of the Complexes.—Electronic spectra were measured in aqueous 0.25 mol dm^{-3} KOH solutions of the complexes in the range 600–190 nm. Infrared spectra of the solids were measured over the range 4000–220 cm^{-1} using KBr discs on a Perkin Elmer 1720 Fourier-transform spectrometer, and Raman spectra using discs of KBr on a Spex Ramalog 5 instrument with 6471 Å irradiation from an Innova 90 Coherent Radiation laser.

Sodium, potassium, copper, silver and gold were determined by atomic absorption spectrometry, the periodate content of the copper, silver and gold complexes by iodometric titration in 0.3 mol dm^{-3} perchloric acid and excess KI using 0.1 mol dm^{-3} $Na_2S_2O_3$, and the iodine content of the palladium and nickel complexes determined as silver iodide after reduction of the complex by sulfur dioxide. Palladium and nickel were determined as dimethylglyoximate[27] from the filtrate from the iodine determination.

Preparation of the Complexes.—Preparations of the copper,[6] silver[6] and gold[7] complexes are modifications of the literature procedures.

$Na_5[Cu\{IO_5(OH)\}_2]\cdot 16H_2O$. Sodium persulfate (0.48 g, 2 mmol) was added to a solution of 0.25 mol dm^{-3} KOH in water (20 cm^3), the mixture heated and stirred with the addition of $CuSO_4\cdot 5H_2O$ (0.5 g, 2 mmol). A blue-black precipitate was formed, which partially dissolved on addition of a solution of periodic acid (0.91 g, 4 mmol) in water (10 cm^3). The resulting brown solution was heated and stirred for 15 min. It was left to cool and filtered to remove the excess of precipitate. A mixture of saturated $NaNO_3$ (5 cm^3) and NaOH (1 mol dm^{-3}, 5 cm^3) solutions in water was added to the filtrate and the resultant mixture was left to crystallise (*ca.* 2 h). The brown precipitate was filtered off, washed with ice-cold water and dried *in vacuo* (Found: H, 3.5; Cu, 7.2; I, 27.8; Na, 11.9. $H_{34}CuI_2Na_5O_{28}$ requires H, 3.7; Cu, 6.9; I, 27.8; Na, 12.5%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 220 (1.26×10^4), 263 (1.06×10^4), 414 (1.00×10^4).

$Na_5[Ag\{IO_5(OH)\}_2]\cdot 12H_2O$. A similar method to the above was used, $Na_2S_2O_8$ being added (0.96 g, 4 mmol) and $AgNO_3$ (0.34 g, 2 mmol) replacing $CuSO_4\cdot 5H_2O$ to produce the orange complex (Found: H, 2.5; Ag, 11.8; I, 28.6; Na, 12.6. $H_{26}AgI_2Na_5O_{24}$ requires H, 2.9; Ag, 12.2; I, 28.6; Na, 13.0%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 221 (2.02×10^4), 249 (1.51×10^4), 356 (1.16×10^4).

$Na_5[Au\{IO_5(OH)\}_2]\cdot 17H_2O$. A similar method to that for the copper complex was used. Less $Na_2S_2O_8$ was added (0.24 g, 1 mmol), while $H[AuCl_4]\cdot nH_2O$ (0.5 g, 1.2 mmol) replaced $CuSO_4\cdot 5H_2O$ to produce the white complex (Found: H, 3.3; Au,

Table 3 Organic Oxidations by Periodato complexes[a]

	$[M(OH)_2\{IO_5(OH)\}_2]^{6-}$							$[M(OH)_2\{IO_5(OH)\}_2]^{6-}$		
	M = Ni^{IV}		M = Pd^{IV}	Pt^{IV}		$[Pd\{IO_5(OH)\}_2]^{6-}$		M = Ru^{VI}		M = Os^{VI}
	A[b]	B[c]	B	A	B	A	B	A	B	A
p-Methoxybenzyl alcohol	7,^{d} 66^e (51)	30^d (21)	82^d (75)	47,^{d} 27^e (72)	79^d (76)	8,^{d} 7^e (14)	16^d (14)	99^{e,f}	79^d (79)	45,^{d} 51^e (950)
o-Methylbenzyl alcohol	13^e (8)	11^d (8)	95^d (95)	18^e (19)	8^d (8)	25,^{d} 18^e (38)	5.5^d (5)	88^e (94)	71^d (71)	98^e (400)
p-Nitrobenzyl alcohol	12,^{d} 28^e (26)	37^d (26)	25^d (26)	5,^{d} 22^e (26)	50^d (49)	10,^{d} 17^e (15)	37^d (34)	83^e (84)	40^d (41)	72^e (400)
3,4-Dimethoxybenzyl alcohol	59,^{d} 6^e [74]	11^d (7)	11^d (11)	57,^{d} 10^e [75]	14^d (13)	53,^{e} 5^d [71]	5,^{e} 6^d (5)	92^e (100)	92^d (93)	99.5^e (1030)
Piperonyl alcohol	22^e (15)	20^d (14)	19^d (17)	54,^{d} 28^e (78)	32^d (32)	78,^{d} 8^e (75)	22^d (20)	91^e (94)	99^d (99)	20,^{d} 72^e (1000)
Cinnamyl alcohol	25,^{d} 18^e (41)	23^d (16)	44^d (40)	15,^{d} 15^e (26)	28^d (28)	14,^{d} 15^e (23)	23^d (20)	13,^{d} 66^e (82)	65^d (65)	19,^{d} 23^e (430)
Benzhydryl alcohol	—	17^g (12)	6^g (6)	—	5^g (5)	—	37^g (33)	40^{f,g}		58^g (400)
α-Tetralol	46^g (32)	26^g (18)	34^g (31)	46^g (45)	27^g (27)	65^g (57)	58^g (52)	85^{f,g}	27^g (27)	7^g (400)
Hydrobenzoin	64,^{d} 33^e (138)	81^d (113)	78^e (150)	58,^{d} 40^e (172)	98^d (190)	48^e (85)	81^d (145)	16,^{d} 70^e (181)		81^e (1670)
Benzaldehyde	90^e (93)			80^e (120)		23^e (20)		96^{e,f}		93^e (1300)
4-Methoxy-benzaldehyde	37^e (25)			20^e (19)		21^e (18)		50^e [60]		
Benzyl bromide	60^e (46)			56^e (55)		53^e (47)		75^e (75)		61^e (100)
p-Methoxybenzyl-chloride	12,^{d} 50^e (43)	47^d (33)	10^d (9)	45,^{d} 31^e (71)	43^d (44)	9,^{d} 21^e (26)	32^d (32)	50,^{d} 48^e (70)	60^d (60)	8,^{d} 88^e (120)
α-Bromo-*p*-xylene	41^e (28)			87^e (85)		60^e (39)		70^e (97)		27^e (275)
1-Bromoethylbenzene	22^d (15)	7^d (4)		26^d (30)	11^d (10)	64^d (60)	7^d (5)	70^d (99)	16^d (16)	22^d (33)
1-Iodobutane	40^e (28)			16^e (15)		11^e (7)		15^e (11)		
2,6-Dichlorobenzyl bromide	32^e (22)			16^e (15)		21^e (18)		10^e (5)		56^d (200)
Bromodiphenyl-methane								50^g (75)		74^g (100)

[a] Percentage yields. Turnovers given in parentheses. Oxidations of alcohols and aldehydes were carried out at room temperature in 3 h, those of alkyl halides in 4 h. [b] In aqueous KOH (0.25 mol dm^{-3}) and KIO_4 (2 mmol). [c] Phase-transfer [1:1 aqueous KOH (0.25 mol dm^{-3})–1,2-dichloromethane with Aliquat 336 (0.5 mmol)]. [d] Corresponding aldehyde. [e] Corresponding acid. [f] Ref. 1. [g] Corresponding ketone.

Table 4 Catalytic oxidations with $[C_5H_5N(CH_2)_{15}CH_3]_4K[IMo_6O_{24}]$ and H_2O_2*

Substrate	Product	Yield (%)	Turnover
p-Methoxybenzyl alcohol	*p*-Methoxybenzaldehyde	46	23
Benzyl alcohol	Benzaldehyde	37	19
Piperonyl alcohol	Piperonaldehyde	46	23
Cinnamyl alcohol	Cinnamaldehyde	41	20
α-Tetralol	α-Tetralone	34	17
Benzhydryl alcohol	Benzophenone	35	17
p-Methoxybenzyl chloride	*p*-Methoxybenzaldehyde	2	1
Benzyl bromide	Benzaldehyde	2	1

* All oxidations performed in 1,2-dichloroethane–H_2O at 50 °C for 3 h; substrate:catalyst ratio 50:1.

18.5; I, 23.6; Na, 11.0. $H_{36}AuI_2Na_5O_{29}$ requires H, 3.4; Au, 18.5; I, 23.8; Na, 10.8%); λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 220 ($1.86 \times 10^4$), 250 (1.30 × 10.4), 347 (85).

$Na_4K[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 15H_2O$. A similar method to that for the preparation of $Na_5[Cu\{IO_5(OH)\}_2]\cdot 16H_2O$ was used in which aqueous 1 mol dm^{-3} NaOH (2 cm^3) was added to the filtrate to produce yellow-green crystals (Found: I, 22.8; K, 7.1; Na, 8.2. $H_{33}AuI_2K_2Na_4O_{28}$ requires I, 23.0; K, 7.1; Na, 8.3%).

$Na_6[Ni(OH)_2\{IO_5(OH)\}_2]\cdot H_2O$. The preparation of this complex was based on the published procedure for '$Na_4H_2[Ni-HIO_6)_2]\cdot 6H_2O$'[12] with some modifications. Solid $Na_3H_2IO_6$ (6 g, prepared by Willard's method[28]) was added to a solution of $Ni(NO_3)_2\cdot 6H_2O$ (0.2 g) in water (30 cm^3), the mixture heated and stirred to 80–90 °C and then oxidised by gradual addition of $K_2S_2O_8$ (5 g). The resulting pale yellow mixture was continuously heated and stirred until it changed to brown. It was left in an ice-bath for 0.5 h and filtered to remove the excess of precipitate (unreacted sodium paraperiodate, potassium persulfate and potassium sulfate). A mixture of saturated $NaNO_3$ (5 cm^3) and NaOH (1 mol dm^{-3}, 5 cm^3) solutions in water was added to the filtrate and the mixture left to crystallise (*ca.* 2 d). The brown microcrystalline precipitate was filtered off, washed with ice-cold water and dried *in vacuo* (Found: I, 36.3; Na, 19.5; Ni, 8.7. $H_6I_2Na_6NiO_{15}$ requires I, 36.5; Na, 19.8; Ni, 8.4%); λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 222 ($8.67 \times 10^3$), 342 (568), 427 (72); IR: 3412–2929s, 2374s, 1652m, 1219s, 1143s, 921m, 737s, 688s, 559s, 339s, 302w cm^{-1}. Raman: 716vs, 682m, 562m, 499m cm^{-1}.

The orange yellow $[Co(en)_3]_2[Ni(OH)_2\{IO_5(OH)\}_2]$ (en = ethane-1,2-diamine) was made by addition of $[Co(en)_3]Cl_3$ to the brown solution of the sodium salt (Found: C, 14.2; H, 5.7; N, 16.4. $C_{12}H_{52}Co_2I_2N_{12}NiO_{14}$ requires C, 14.1; H, 5.1; N, 16.5%); IR: 3450–2700s, 2404m, 1607s, 1174m, 1058s, 752s, 577s, 542m, 452w, 408w, 374w cm^{-1}; Raman: 1466w, 1166w, 1126s, 760m, 602w, 542m, 454w, 376m, 230s cm^{-1}.

$Na_6[Pd(OH)_2\{IO_5(OH)\}_2]\cdot 10H_2O$. This complex was prepared by the literature method.[13] Palladium(II) chloride (0.4 g, 2.26 mmol) was dissolved in hot water (3 cm^3) containing seven drops of concentrated hydrochloric acid and then cooled to room temperature. Chlorine gas was bubbled through the solution until a deep red colour persisted. After passing nitrogen through the solution, $NaIO_4$ (1.14 g, 4.6 mmol) was added with NaOH (0.32 g, 8 mmol) and the mixture was boiled until orange crystals were produced. The mixture was cooled and left to stand overnight producing a red orange precipitate. It was filtered off, washed with ice-cold water, ethanol and diethyl ether and dried in air (Found: H, 2.2; I, 27.7; Na, 14.2; Pd, 11.6. $H_{24}I_2Na_6O_{24}Pd$ requires H, 2.6; I, 28.0; Na, 15.2; Pd, 11.7%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 231 (2.16×10^3), 288 (1.81×10^3), 330 (1.72×10^3).

$Na_6[Pd\{IO_5(OH)\}_2]\cdot 11H_2O$. This new complex was prepared from $Na_2[PdCl_4]$ (0.32 g, 1 mmol), added to a solution of 0.25 mol dm^{-3} NaOH in water (15 cm^3) and the mixture stirred with the addition of a solution of periodic acid (0.46 g, 2 mmol) in water (5 cm^3). The resulting yellow-brown solution was stirred until a yellow precipitate formed. This was filtered off, washed with cold water and dried *in vacuo* (Found: I, 28.4; Na, 15.3; Pd, 11.8. $H_{24}I_2Na_6O_{23}Pd$ requires I, 28.5; Na, 15.5; Pd, 12.0%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 223 (2.32×10^4), 288 (5.81×10^3); IR: 3400–2800s, 2261m, 1652s, 716s, 607m, 559m, 495m, 395s cm^{-1}; Raman: 740s, 608s, 564s, 464m, 346m, 267m cm^{-1}.

The orange compound $[Co(en)_3]_2[Pd\{IO_5(OH)\}_2]\cdot 3H_2O$ was made by addition of $[Co(en)_3]Cl_3$ to the yellow solution of the sodium salt (Found: C, 13.3; H, 5.1; N, 14.7. $C_{12}H_{56}Co_2I_2N_{12}O_{15}Pd$ requires C, 13.3; H, 5.2; N, 15.5%); IR: 3500–2800s, 2410m, 1586s, 1162s, 733s, 618w, 565w, 528w, 399s, 294w cm^{-1}; Raman: 1467w, 1164w, 753m, 612m, 531s, 448s, 377m, 277s cm^{-1}.

$K_6[Pt(OH)_2\{IO_5(OH)\}_2]\cdot 10H_2O$. The complex was prepared by the literature method.[13] The salt $K_2[PtCl_4]$ (0.22 g, 0.46 mmol) in water (15 cm^3) was added to KOH (0.28 g, 5 mmol) in water (1 cm^3). Then KIO_4 (0.22 g, 0.94 mmol) and KOH (1.25 g) were added and the mixture boiled to concentrate the pale yellow solution. The solution was cooled to −18 °C and the resulting pale yellow crystals filtered off, washed with ice-cold water, ethanol and diethyl ether and dried in air (Found: H, 2.1; I, 23.0; K, 20.7. $H_{24}I_2K_6O_{24}Pt$ requires H, 2.2; I, 23.2; K, 21.5%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 223 (2.71×10^4).

$Na_6[Pt(OH)_2\{IO_5(OH)\}_2]\cdot 14H_2O$. The salt $K_2[PtCl_4]$ (0.4 g, 1 mmol) was added to 0.2 mol dm^{-3} KOH solution (15 cm^3), the mixture heated and stirred with the addition of periodic acid (0.46 g, 2 mmol) in water (5 cm^3). The solution slowly turned yellow. It was boiled for about 15 min and left to cool. A mixture of saturated $NaNO_3$–NaOH (1 mol dm^{-3}) (1:1) solutions in water (10 cm^3) was added to the reaction mixture. The pale yellow solution formed was cooled to −18 °C and the resulting yellow precipitate was filtered off, washed with ice-cold water, ethanol, diethyl ether and dried in air (Found: H, 2.8; I, 24.2; Na, 12.2. $H_{32}I_2Na_6O_{28}Pt$ requires H, 3.0; I, 23.8; Na, 12.9%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 224 (2.81×10^4).

$Na_6[RuO_2\{IO_5(OH)\}_2]\cdot 18H_2O$. This is a modification of our previously reported procedure.[1] Hydrated ruthenium chloride (0.52 g, 2 mmol) in water (30 cm^3) was stirred with sufficient 2 mol dm^{-3} aqueous NaOH to give a black precipitate of RuO_2. Sodium persulfate (0.6 g, 2.5 mmol) was added with stirring until a red brown solution was obtained. Sodium periodate (0.85 g, 9 mmol) in water (3 cm^3) was added and a red brown precipitate appeared at once. It was filtered off, washed with a little water and dried *in vacuo* (Found: H, 3.5; Na, 13.0; I, 24.2. $H_{38}I_2Na_6O_{32}Ru$ requires H, 3.6; Na, 13.2; I, 24.4%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 221 (9.24×10^3), 389 (1.88×10^3).

$Na_6[OsO_2\{IO_5(OH)\}_2]\cdot 18H_2O$. This preparation differs slightly from that given in the literature.[14] To a stirred solution of KOH (0.09 g, 1.7 mmol) and KIO_4 (0.23 g, 1 mmol) in water (9 cm^3) was added *trans*-$K_2[OsO_2(OH)_4]$ (0.18 g, 0.5 mmol). A red-brown solution was obtained to which a saturated solution of $NaNO_3$ (0.3 g, 3.5 mmol) in water (1 cm^3) was added. The stirring was stopped and the mixture placed in a refrigerator for 2 h. The resulting yellow precipitate was filtered off, washed with ice-cold water (3 cm^3) and dried *in vacuo*. Yield 0.42 g, 0.38 mmol (76%) (Found: Na, 12.1; Os, 16.8. $H_{38}I_2Na_6O_{32}Os$ requires Na, 12.2; Os, 16.8%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 217 (7.58×10^3), 320 (2.04×10^3), 405 (679).

$K_5[IMo_6O_{24}]\cdot 6H_2O$. This compound was prepared by a method based on that of Blomstrand.[17] Molybdenum(VI) oxide (3.2 g, 22.2 mmol), K_2CO_3 (0.52 g, 3.76 mmol) and KIO_4 (1.08 g, 4.70 mmol) were dissolved in water by heating to near boiling point. The small amount of undissolved material was filtered off, and the light yellow filtrate evaporated down by heating on a water-bath to yield a light yellow microcrystalline solid (Found: K, 13.9. $H_{12}IK_5Mo_6O_{30}$ requires K, 14.1%).

The pale cream compound $[C_5H_5N(CH_2)_{15}CH_3]_4K[IMo_6O_{24}]$ was made from hexadecylpyridinium chloride monohydrate (3.04 g, 8.5 mmol) in water (50 cm^3) and a stirred solution of $K_5[IMo_6O_{24}]\cdot 6H_2O$ (2.78 g, 2.0 mmol) in water (25 cm^3). The precipitate was filtered off, washed with water (2 × 10 cm^3) and dried *in vacuo* (Found: C, 42.2; H, 6.9; N, 2.25. $C_{84}H_{152}IKMo_6N_4O_{24}$ requires C, 43.0; H, 6.5; N, 2.4%).

$K_5[IW_6O_{24}]\cdot 6H_2O$ *and* $[C_5H_5N(CH_2)_{15}CH_3]_4K[IW_6O_{24}]$. Tungstic acid ($WO_3\cdot H_2O$) (5.55 g, 22.2 mmol), K_2CO_3 (0.52 g, 3.76 mmol) and KIO_4 (1.08 g, 4.70 mmol) were dissolved in water (200 cm^3) by heating to near boiling point. The undissolved solid was filtered off and the colourless filtrate evaporated to give $K_5[IW_6O_{24}]\cdot 6H_2O$ as a white solid (Found: K, 10.5. $H_{12}K_5IO_{30}W_6$ requires K, 10.2%). The hexadecylpyridinium salt was prepared as a cream solid in a similar manner to that for the molybdenum analogue (Found: C, 35.4; H, 5.5; N, 1.9. $C_{84}H_{152}IKN_4O_{24}W_6$ requires C, 35.1; H, 5.3; N, 2.0%).

Organic Oxidations.—Stoichiometric. Reactions were carried out using $[M\{IO_5(OH)\}_2]^{5-}$ (M = Cu, Ag or Au), $[M(OH)_2\{IO_5(OH)\}_2]^{6-}$ (M = Ni or Pt), $[Pd\{IO_5(OH)\}_2]^{6-}$, *trans*-$[MO_2\{IO_5(OH)\}_2]^{6-}$ (M = Ru or Os) with 0.5 mmol of complex and 1.5 mmol of the organic substrate in aqueous KOH (0.25 mol dm^{-3}, 20 cm^3). The mixture was stirred at room temperature over 1–3 h (alcohols and aldehydes) or 4 h (alkyl halides) periods, then filtered and extracted with diethyl ether (3 × 20 cm^3). The ethereal layer was then dried with anhydrous Na_2SO_4 and its aldehyde or ketone content quantified with 2,4-dinitrophenylhydrazine. The alkaline aqueous layer was acidified with H_2SO_4 (5 mol dm^{-3}) to pH 2, extracted with diethyl ether (3 × 20 cm^3) and dried to give the acid.

Catalytic. For catalytic oxidations by $[M(OH)_2\{IO_5(OH)\}_2]^{6-}$ (M = Ni or Pt) $[Pd\{IO_5(OH)\}_2]^{6-}$ or *trans*-$[RuO_2\{IO_5(OH)\}_2]^{6-}$ in aqueous solutions, 0.01 mmol of catalyst was dissolved in 0.25 mol dm^{-3} aqueous KOH (20 cm^3), KIO_4 (0.506 g, 2.2 mmol) and the substrate (1 mmol) and the reaction mixture stirred for 3 h at room temperature. The products were then extracted and treated as above.

For phase-transfer oxidations Aliquat 336 (tricaprylmethylammonium chloride) (0.2 g) was added to the reaction mixture together with 1,2-dichloroethane (20 cm^3). For biphasic oxidations using $[C_5H_5N(CH_2)_{15}CH_3]_4K[IMo_6O_{24}]$ and H_2O_2 the method for *p*-methoxybenzyl alcohol is typical.

p-Methoxybenzyl alcohol (0.14 g, 1.0 mmol) and $[C_5H_5N(CH_2)_{15}CH_3]_4K[IMo_6O_{24}]$ (0.047 g, 0.02 mmol) were dissolved in 1,2-dichloroethane (10 cm^3). Hydrogen peroxide (15%, 10 cm^3) was added and the mixture stirred vigorously at 80 °C for 3 h. The organic phase was dried over anhydrous magnesium sulfate and filtered through silica gel H. Evaporation to dryness gave the product, and its aldehyde or ketone content was quantified with 2,4-dinitrophenylhydrazine.

Crystal-structure Determination of $Na_4K[Au\{IO_5(OH)\}_2]\cdot KOH\cdot 5H_2O$.—*Crystal data.* $H_{33}AuI_2K_2Na_4O_{28}$, $M = 1102.2$, triclinic, space group $P\bar{1}$, $a = 6.791(2)$, $b = 7.196(2)$, $c = 13.877(2)$ Å, $\alpha = 82.12(2)$, $\beta = 82.01(2)$, $\gamma = 81.95(2)°$, $U = 660.2(2)$ Å^3, $Z = 1$, $D_c = 2.77$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.710\,73$ Å), μ(Mo-Kα) = 84 cm^{-1}, $F(000) = 524$.

Data collection and processing. Data were measured on a Siemens P4/PC diffractometer with Mo-Kα radiation (graphite monochromator) using ω scans. A crystal of dimensions 0.28 × 0.28 × 0.32 mm was cut from the centre of a partially decomposed cluster and coated with epoxy resin to prevent further decomposition. 2325 Independent reflections ($2\theta < 50°$) were measured of which 2232 had $|F_o| > 4\sigma|F_o|$ and were considered observed. The data were corrected for Lorentz and polarisation factors and an empirical absorption correction based upon 350 azimuthal measurements was applied (maximum and minimum transmission factors 0.077 and 0.057). The determination was carried out at room temperature.

Structure analysis and refinement. The structure was solved by the heavy-atom method. Some of the water molecules were judged to have only partial site occupancies: O(13), O(14A) and O(14B), 50%, O(15A) and O(15B), 25%. The full and half-weight non-hydrogen atoms were refined anisotropically, the quarter-weight atoms isotropically. The hydrogen atoms could not be definitively located and were omitted from the refinement process. Refinement was by full-matrix least squares to $R = 0.035$, $R' = 0.041$ [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 1.58 and −1.88 e Å^{-3} in the region of the Au atom. The mean and maximum shift/error in the final refinement were 0.037 and 0.328 respectively. Computations were carried out on an IBM model 70 386 PC using the SHELXTL PC program system.[29]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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