

# Oxo osmium(VIII) complexes in oxidation: crystal structures of $\text{OsO}_4 \cdot \text{nmo}$ ( $\text{nmo} = N\text{-methylmorpholine } N\text{-oxide}$ ) and $\text{OsO}_4 \cdot \text{mmm}$ ( $\text{mmm} = N\text{-methylmorpholine}$ ), and use of $\text{cis-}[\text{OsO}_4(\text{OH})_2]^{2-}$ as an oxidation catalyst†

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The new complexes  $\text{OsO}_4 \cdot \text{nmo}$  ( $\text{nmo} = N\text{-methylmorpholine } N\text{-oxide}$ ) and  $\text{OsO}_4 \cdot \text{mmm}$  ( $\text{mmm} = N\text{-methylmorpholine}$ ) have been made, their crystal structures determined, and their possible involvement in the catalysed dihydroxylation of alkenes considered. The use of  $\text{cis-}[\text{OsO}_4(\text{OH})_2]^{2-}$  as a catalyst for the oxidation of alcohols, aldehydes and alkyl halides to carboxylic acids with  $[\text{Fe}(\text{CN})_6]^{3-}$  and other co-oxidants and also for the cleavage and dihydroxylation of alkenes with  $[\text{Fe}(\text{CN})_6]^{3-}$  has been investigated.

There is currently much interest and controversy surrounding the processes involved in the dihydroxylation of alkenes catalysed by osmium tetroxide,  $\text{OsO}_4$ .<sup>2-4</sup> The co-oxidant of choice is  $N\text{-methylmorpholine } N\text{-oxide}$  ( $\text{nmo}$ );<sup>4</sup> for asymmetric dihydroxylation, however,<sup>5,6</sup>  $[\text{Fe}(\text{CN})_6]^{3-}$  or a mixture<sup>7</sup> of  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $\text{S}_2\text{O}_8^{2-}$  were found to be more effective co-oxidants.

Here we report an investigation of catalyst-co-oxidant interactions in oxidations effected by  $\text{OsO}_4$  with  $\text{nmo}$ , and also explore the possible uses of another osmium(VIII) species,  $\text{cis-}[\text{OsO}_4(\text{OH})_2]^{2-}$ , as an oxidation catalyst with  $[\text{Fe}(\text{CN})_6]^{3-}$  and other co-oxidants. The intermediacy of  $\text{cis-}[\text{OsO}_4(\text{OH})_2]^{2-}$  has been suggested in the reaction between  $\text{OsO}_4$  or  $\text{trans-}[\text{OsO}_2(\text{OH})_4]^{2-}$  and catalytic systems in which  $[\text{Fe}(\text{CN})_6]^{3-}$  is the co-oxidant in alkaline water-*tert*-butyl alcohol mixtures.<sup>4,8</sup>

## Results and Discussion

### (a) Preparation and crystal structure of $\text{OsO}_4 \cdot \text{nmo}$

The first reported use of  $\text{nmo}$  as a co-oxidant for the dihydroxylation of alkenes with  $\text{OsO}_4$  was in 1976,<sup>9</sup> and it rapidly became the co-oxidant of choice for these reactions.<sup>4</sup> Despite the debate as to the mechanism of the dihydroxylation of alkenes by  $\text{OsO}_4$ ,<sup>2-4</sup> little attention has been paid to the role of the co-oxidant.

We find that  $\text{OsO}_4$  reacts with  $\text{nmo}$  in  $\text{CH}_2\text{Cl}_2$  to give an unstable but isolable orange 1:1 complex  $\text{OsO}_4 \cdot \text{nmo}$  and present here its single-crystal structure (Fig. 1). This is the first time that a complex of a co-oxidant with its associated catalyst in the dihydroxylation of alkenes has been isolated and structurally characterised, and its existence clearly has implications for the mechanism of the catalytic processes involving these components. The structure is also of interest because there are two potential co-ordination sites on  $\text{nmo}$ , the *exo* oxygen and the ring oxygen atoms.

† This paper is dedicated to the fond memory of Geoff, as he was always called during his forty years at I.C. Through all those years he never lost his love and enthusiasm for chemistry and, above all, he never lost his sense of fun.

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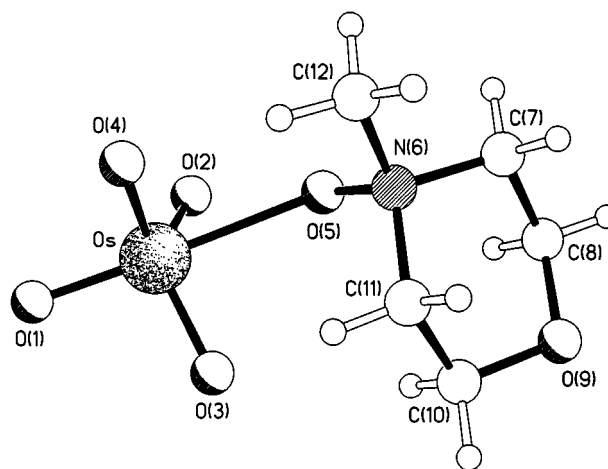
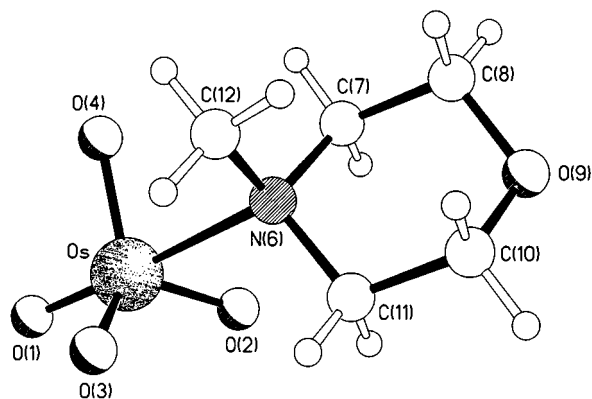
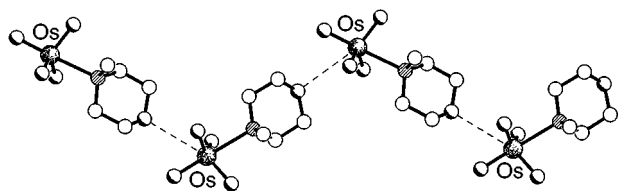


Fig. 1 Molecular structure of  $\text{OsO}_4 \cdot \text{nmo}$

The X-ray analysis confirms the 1:1 stoichiometry of the complex and shows (Fig. 1) the co-oxidant to be co-ordinated to the osmium centre *via* the pendant oxygen atom O(5) rather than the ring oxygen atom O(9). [The structure contains a small rotational disorder (55:45) of the trio of equatorial oxygen atoms; the osmium atom,  $\text{nmo}$  ligand and axial oxygen atom are all ordered.] The geometry at osmium is distorted trigonal bipyramidal, the initial tetrahedral  $\text{OsO}_4$  unit having undergone a typical<sup>2a,3b,10,11</sup> facial compression to accommodate the *exo*-oxygen atom of the  $\text{nmo}$  ligand. The osmium atom lies 0.32 Å out of the equatorial plane towards the axial oxo ligand O(1), which surprisingly has a slightly longer Os–O distance [1.729(6) Å] (Table 1) than its equatorial counterparts (*ca.* 1.71 Å). The Os–O(5) bond length is, as expected, long at 2.305(4) Å, but is noticeably shorter than those seen in other  $\text{OsO}_4 \cdot \text{L}$  adducts.<sup>2a,3b,10,11</sup> This may be due to the presence of a formal negative charge on the ligand oxygen atom, which in turn contributes to the lengthening of the *trans*-axial bond to O(1) (see above). There is an associated slight lengthening of the N–O bond distance [1.414(7) Å] within the  $\text{nmo}$  ligand, *cf.* its value [1.391(3) Å] in unco-ordinated  $\text{nmo}$  monohydrate.<sup>12</sup> There are no notable intermolecular interactions.

**Table 1** Selected bond lengths (Å) and angles (°) for OsO<sub>4</sub>·nmo

Os–O(1)	1.729(6)	Os–O(2)	1.705(5)
Os–O(3)	1.703(5)	Os–O(4)	1.710(5)
Os–O(5)	2.305(4)	O(5)–N(6)	1.414(7)
O(1)–Os–O(2)	101.8(4)	O(1)–Os–O(3)	101.1(5)
O(1)–Os–O(4)	99.4(5)	O(1)–Os–O(5)	175.1(3)
O(2)–Os–O(3)	118.0(3)	O(2)–Os–O(4)	115.5(3)
O(2)–Os–O(5)	73.3(3)	O(3)–Os–O(4)	116.2(3)
O(3)–Os–O(5)	81.7(4)	O(4)–Os–O(5)	82.7(4)
Os–O(5)–N(6)	128.7(3)		

**Fig. 2** Molecular structure of OsO<sub>4</sub>·nmm**Fig. 3** The loosely linked chains of complexes present in the structure of OsO<sub>4</sub>·nmm**(b) Preparation and crystal structure of OsO<sub>4</sub>·nmm**

Since in the OsO<sub>4</sub>·nmo catalytic reaction *N*-methylmorpholine (nmm) must be released and could then function as a competitive ligand we attempted to isolate an OsO<sub>4</sub>·nmm complex. The structure of such a species would have added interest because, as with nmo, there are two potential co-ordination sites, the ring oxygen and nitrogen atoms. We find that reaction of OsO<sub>4</sub> with nmm in diethyl ether solution gives unstable yet isolable red crystals of a 1 : 1 adduct, OsO<sub>4</sub>·nmm.

The X-ray analysis shows (Fig. 2) the nmm to be co-ordinated to the osmium centre *via* the hindered nitrogen atom N(6) rather than *via* the more accessible ring oxygen atom O(9). As in OsO<sub>4</sub>·nmo, the co-ordination geometry is again characteristically distorted trigonal bipyramidal, the osmium atom lying 0.35 Å out of the equatorial plane towards the axial oxo ligand. In contrast to OsO<sub>4</sub>·nmo, here both the axial and equatorial Os–O distances are essentially the same, ranging between 1.708(6) and 1.713(7) Å (Table 2), distances similar to those observed in OsO<sub>4</sub>.<sup>13</sup> The Os–N distance of 2.440(7) Å is, as expected, long, but comparable with those observed in, for example, [OsO<sub>4</sub>(quin)] (quin = quinuclidine);<sup>10</sup> [OsO<sub>4</sub>(napy)] (napy = 1,8-naphthyridine),<sup>11</sup> and recently described adducts of OsO<sub>4</sub> with 4-pyrrolidino-, 4-phenyl- and 4-cyano-pyridines.<sup>2a</sup> Similar long Os–N distances are found in N-donor adducts<sup>14</sup> with imido complexes [OsO<sub>3</sub>(NR)] made by Sharpless and co-workers<sup>15</sup> and Wilkinson *et al.*<sup>16</sup> Although there are no dominant intermolecular interactions, it is interesting that one of the ring oxygen lone pairs in one molecule is directed almost orthogonally (84°) into one of the OsO<sub>4</sub> ‘tetrahedral’ faces in another, an approach analogous to that of the co-ordinated

**Table 2** Selected bond lengths (Å) and angles (°) for OsO<sub>4</sub>·nmm

Os–O(1)	1.708(6)	Os–O(2)	1.713(7)
Os–O(3)	1.708(6)	Os–O(4)	1.709(6)
Os–N(6)	2.440(7)		
O(1)–Os–O(2)	102.9(3)	O(1)–Os–O(3)	101.8(3)
O(1)–Os–O(4)	101.0(3)	O(1)–Os–N(6)	177.7(3)
O(2)–Os–O(3)	116.8(4)	O(2)–Os–O(4)	115.5(3)
O(2)–Os–N(6)	79.2(3)	O(3)–Os–O(4)	115.3(3)
O(3)–Os–N(6)	78.1(3)	O(4)–Os–N(6)	77.1(3)

nitrogen. The O···Os distance is long at 3.34 Å (the distance of this oxygen atom from the tetrahedral face is 2.71 Å) indicating a weak electrostatic interaction with the osmium centre, producing a loosely linked zigzag chain of molecules that extends in the crystallographic *b* direction (Fig. 3).

**(c) OsO<sub>4</sub>·nmo and OsO<sub>4</sub>·nmm in solution**

Infrared spectra of solutions of OsO<sub>4</sub>·nmo and OsO<sub>4</sub>·nmm show bands near 950 and 920 cm<sup>−1</sup>, not present for nmo or nmm, which we assign to ν(OsO) stretches, as observed in other OsO<sub>4</sub>·L species;<sup>17</sup> unfortunately laser-induced decomposition prevented acquisition of good Raman data. The asymmetric stretch of free OsO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> is obscured by the 950 cm<sup>−1</sup> bands. Again, as with other OsO<sub>4</sub>·L adducts,<sup>17</sup> it is probable that in solution a mixture of OsO<sub>4</sub> and OsO<sub>4</sub>·L (L = nmo or nmm) is present.

The likelihood of the presence of OsO<sub>4</sub>·nmo and OsO<sub>4</sub>·nmm (the latter being produced by the nmm released after reoxidation of Os<sup>VI</sup> to Os<sup>VIII</sup> in the catalytic OsO<sub>4</sub>–alkene–nmo cycle) means that these species are likely to play a role in the dihydroxylation of alkenes by OsO<sub>4</sub> when nmo is the co-oxidant. A similar intermediacy of isolated catalyst–co-oxidant complexes has been postulated for manganese–H<sub>2</sub>tpp complexes (H<sub>2</sub>tpp = 5,10,15,20-tetraphenylporphyrin) adducts with iodosylbenzene<sup>18</sup> and nmo<sup>19</sup> in alkene epoxidation reactions catalysed by these species.

**(d) *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2−</sup> as a catalyst for organic oxidations**

The use of OsO<sub>4</sub> or *trans*-[OsO<sub>2</sub>(OH)<sub>4</sub>]<sup>2−</sup> in aqueous *tert*-butyl alcohol media with [Fe(CN)<sub>6</sub>]<sup>3−</sup>–<sup>5,6</sup> or <sup>4</sup>[Fe(CN)<sub>6</sub>]<sup>3−</sup>–S<sub>2</sub>O<sub>8</sub><sup>2−</sup> as co-oxidants, and the possible implication of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2−</sup> in such reactions,<sup>4,8</sup> prompted us to undertake a study of this complex as an oxidation catalyst.

Salts of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2−</sup> are made by reaction of OsO<sub>4</sub> with the appropriate aqueous alkali.<sup>20</sup> The single-crystal structures of the lithium<sup>21</sup> and sodium<sup>22</sup> salts confirmed the *cis* structure of the anion; the reasons for this geometry have been discussed.<sup>23</sup> Infrared data for the normal and deuterated salts<sup>24,25</sup> and the electronic spectrum of the anion in aqueous base<sup>26</sup> have been reported. The first report of the use of OsO<sub>4</sub> in base as an oxidation catalyst with [Fe(CN)<sub>6</sub>]<sup>3−</sup> as co-oxidant was by Solomyi in 1956;<sup>27</sup> later it was shown that *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2−</sup> with [Fe(CN)<sub>6</sub>]<sup>3−</sup> as co-oxidant oxidised ethylene, propylene and 2-methylpropylene to the corresponding glycols.<sup>26</sup> The only other preparative use in the literature of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2−</sup> as an oxidation catalyst reported is in the oxidation of mandelic acid [PhCH(OH)CO<sub>2</sub>H] using [Fe(CN)<sub>6</sub>]<sup>3−</sup> as co-oxidant.<sup>28,29</sup> There are a number of papers on the kinetics of a variety of organic oxidation reactions with this anion as a catalyst in the presence of a number of co-oxidants.<sup>30–33</sup>

**(i) Oxidation of alcohols, aldehydes, alkyl halides and benzylamines.** Solutions of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2−</sup> were made from OsO<sub>4</sub> and molar aqueous NaOH or KOH. Profiles of their Raman spectra were similar to that of solid *cis*-Cs<sub>2</sub>[OsO<sub>4</sub>(OH)<sub>2</sub>], suggesting that the same anion was present in both, and the electronic spectrum was similar to that reported.<sup>26</sup> The results in Table 3 show that *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2−</sup> under ambient

**Table 3** Oxidations catalysed by *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>

Substrate	Product	Co-oxidant	Yield (%)	Turnover <sup>a</sup>	Time (h)
<b>Alcohols</b>					
Benzyl alcohol	Benzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	84	21	3
	Benzoic acid	BrO <sub>3</sub> <sup>-</sup>	63	16	3
	Benzoic acid	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	61	16	3
<i>p</i> -Methoxybenzyl alcohol	<i>p</i> -Methoxybenzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	80	21	3
	<i>p</i> -Methoxybenzoic acid	BrO <sub>3</sub> <sup>-</sup>	75	19	3
	<i>p</i> -Methoxybenzoic acid	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	50	15	3
4-Methylbenzyl alcohol	4-Methylbenzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	85	22	3
	4-Methylbenzoic acid	BrO <sub>3</sub> <sup>-</sup>	66	17	3
Cinnamyl alcohol	Benzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	85	22	3
	Benzoic acid	BrO <sub>3</sub> <sup>-</sup>	48	12	6
	Benzoic acid	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	11	3	3
Piperonyl alcohol	Piperonylic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	90	23	3
	Piperonylic acid	BrO <sub>3</sub> <sup>-</sup>	75	19	6
<i>p</i> -Nitrobenzyl alcohol	<i>p</i> -Nitrobenzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	85	22	3
	<i>p</i> -Nitrobenzoic acid	BrO <sub>3</sub> <sup>-</sup>	45	11	6
2-Hydroxybenzyl alcohol	Salicylic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	75	19	3
	Salicylic acid	BrO <sub>3</sub> <sup>-</sup>	54	14	3
3,4-Dimethoxybenzyl alcohol	3,4-Dimethoxybenzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	66	17	3
	3,4-Dimethoxybenzoic acid	BrO <sub>3</sub> <sup>-</sup>	41	10	6
<b>Aldehydes</b>					
Benzaldehyde	Benzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	82	21	3
	Benzoic acid	BrO <sub>3</sub> <sup>-</sup>	66	17	3
	Benzoic acid	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	25	6	3
<i>p</i> -Nitrobenzaldehyde	<i>p</i> -Nitrobenzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	75	19	3
	<i>p</i> -Nitrobenzoic acid	BrO <sub>3</sub> <sup>-</sup>	60	15	3
<b>Alkyl halides</b>					
Benzyl chloride	Benzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	50	13	10
	Benzoic acid	BrO <sub>3</sub> <sup>-</sup>	61	15	10
Benzyl bromide	Benzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	61	15	6
	Benzoic acid	BrO <sub>3</sub> <sup>-</sup>	78	20	6
Cinnamyl bromide	Cinnamic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	51	13	10
<b>Alkenes</b>					
Styrene	Benzoic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	65	17	24
	Styrene-1,3-diol <sup>b</sup>	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	60	30	24
Cyclohexene	Adipic acid	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	51	13	24

<sup>a</sup> Turnover = moles of product/moles of catalyst. Reactions carried out using aqueous 1 M NaOH, 2 × 10<sup>-3</sup> M *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>, 0.6 M [Fe(CN)<sub>6</sub>]<sup>3-</sup> and 0.2 M BrO<sub>3</sub><sup>-</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. <sup>b</sup> Reaction in 0.1 M KOH.

conditions in aqueous molar base catalyses the oxidation of primary alcohols, aldehydes and of benzylic halides to carboxylic acids, using either [Fe(CN)<sub>6</sub>]<sup>3-</sup>, BrO<sub>3</sub><sup>-</sup> or S<sub>2</sub>O<sub>8</sub><sup>2-</sup> as co-oxidants. In all cases 'blank' oxidations were carried out in the absence of osmium catalyst and little or no oxidation product was found.

The ability of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> to oxidise primary alcohols to carboxylic acids is similar to that of *trans*-[Ru(OH)<sub>2</sub>O<sub>3</sub>]<sup>2-</sup> which will effect such oxidations with [Fe(CN)<sub>6</sub>]<sup>3-</sup> or, more effectively, persulfate as co-oxidant.<sup>34</sup> We find however that *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> is a poor oxidant for secondary alcohols and for alkyl halides is an inferior oxidant to the *trans*-[Ru(OH)<sub>2</sub>O<sub>3</sub>]<sup>2-</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system.<sup>34</sup> As with the latter reagent the *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>-BrO<sub>3</sub><sup>-</sup> and -S<sub>2</sub>O<sub>8</sub><sup>2-</sup> systems are self-indicating: when the substrate is added the orange colour of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> changes to that of the violet *trans*-[Os<sup>VI</sup>O<sub>2</sub>(OH)<sub>4</sub>]<sup>2-</sup> (identified by its known<sup>35</sup> electronic spectrum) returning to orange only when the oxidation is complete. It is noteworthy that the reagent cleaves cinnamic acid to benzoic acid, as does [RuO<sub>4</sub>]<sup>-</sup>-BrO<sub>3</sub><sup>-</sup>.<sup>34</sup> This is consistent with the observation of Kumar and Mathur<sup>36</sup> that *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> in the presence of [Fe(CN)<sub>6</sub>]<sup>3-</sup> in base cleaves cinnamate to benzoate.

A large-scale oxidation of benzyl alcohol (5.5 g, 50 mmol) with the *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>-BrO<sub>3</sub><sup>-</sup> reagent over 5 h at room temperature gave benzoic acid (5.2 g, 85%). Since [Fe(CN)<sub>6</sub>]<sup>3-</sup> and, to a lesser extent, BrO<sub>3</sub><sup>-</sup> are more effective co-oxidants with *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> than with persulfate, the latter was not

used further in this work. Disappointingly, nmo was not an effective co-oxidant for this system.

Attempts to use the *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>-[Fe(CN)<sub>6</sub>]<sup>3-</sup> system to oxidise benzylamine and 4-methoxybenzylamine to the corresponding nitriles gave a mixture of the nitrile and the corresponding carboxylic acid; *trans*-[Ru(OH)<sub>2</sub>O<sub>3</sub>]<sup>2-</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is more effective in this respect, giving good yields of nitriles without acid contaminant.<sup>37</sup> Although kinetic data have been reported for various organic oxidations catalysed by *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> with periodate as co-oxidant<sup>38,39</sup> in base we find that use of this co-oxidant is impracticable on a preparative scale: periodate salts are too insoluble in aqueous base to allow sufficient concentrations of co-oxidant to be maintained.

**(ii) Oxidation of alkenes.** In preliminary work we have attempted to effect dihydroxylations of styrene and cyclohexene using *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>-[Fe(CN)<sub>6</sub>]<sup>3-</sup> in molar and also in 0.1 M KOH solution, using the experimental procedure of Sharpless and co-workers<sup>40</sup> for dihydroxylation of alkenes with hydroquinidine 4-chlorobenzoate as accelerator, 1 or 0.1 M KOH replacing K<sub>2</sub>CO<sub>3</sub> in a water-*tert*-butyl alcohol mixture. In molar aqueous KOH solution cleavage occurred to give benzoic and adipic acids respectively, but in 0.1 M KOH dihydroxylation does occur, giving styrene-2,3-diol in 60% yield and cyclohexane-1,2-diol in 17% yield respectively. This is in agreement with the observation of Mayell<sup>26</sup> that dihydroxylation of propene by *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> with [Fe(CN)<sub>6</sub>]<sup>3-</sup> is more effective in 0.1 M than in 1 M base.

Although as mentioned above *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> has been suggested as an intermediate in the Sharpless asymmetric dihydroxylation procedure using [Fe(CN)<sub>6</sub>]<sup>3-</sup> in water-*tert*-butyl alcohol with K<sub>2</sub>CO<sub>3</sub> at *ca.* pH 10, we were unable to detect any significant quantities of the material under these conditions by electronic spectroscopy. Indeed our electronic spectroscopic studies show that the only osmium(VIII) species present in such solutions is OsO<sub>4</sub>.

## Conclusion

We have prepared and structurally characterised the adducts OsO<sub>4</sub>·nmo and OsO<sub>4</sub>·nmm; both are likely to be involved in the dihydroxylation of alkenes by OsO<sub>4</sub> with nmo as co-oxidant. An exploration of the capability of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> as an oxidation catalyst for a variety of organic substrates with [Fe(CN)<sub>6</sub>]<sup>3-</sup>, bromate and persulfate as co-oxidants shows that the first is the most effective. Preliminary data also suggest that the *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>-[Fe(CN)<sub>6</sub>]<sup>3-</sup> reagent will cleave alkenes in strong (molar) base and dihydroxylate them in weaker 0.1 M base.

## Experimental

### X-Ray crystallography

**Crystal data.** For OsO<sub>4</sub>·nmo. C<sub>5</sub>H<sub>11</sub>NO<sub>6</sub>Os, *M* = 371.4, monoclinic, space group *P2<sub>1</sub>/c* (no. 14), *a* = 9.021(1), *b* = 14.690(1), *c* = 6.965(1) Å, β = 91.64(1)°, *U* = 922.6(2) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 2.674 g cm<sup>-3</sup>, μ(Mo-Kα) = 138.2 cm<sup>-1</sup>, λ = 0.710 73 Å, *F*(000) = 688. An orange prism of dimensions 0.27 × 0.27 × 0.13 mm was used.

For OsO<sub>4</sub>·nmm. C<sub>5</sub>H<sub>11</sub>NO<sub>5</sub>Os, *M* = 355.4, orthorhombic, space group *Pbca* (no. 61), *a* = 7.074(2), *b* = 13.801(3), *c* = 17.343(3) Å, *U* = 1693.1(6) Å<sup>3</sup>, *Z* = 8, *D<sub>c</sub>* = 2.788 g cm<sup>-3</sup>, μ(Cu-Kα) = 284.2 cm<sup>-1</sup>, λ = 1.541 78 Å, *F*(000) = 1312. A red plate of dimensions 0.20 × 0.13 × 0.03 mm was used.

**Data collection and processing.** Both complexes are unstable at room temperature so the crystals were immersed in oil and data were measured at 153 K using Siemens P4/PC diffractometers with graphite-monochromated radiation [Mo-Kα for OsO<sub>4</sub>·nmo and Cu-Kα (rotating anode source) for OsO<sub>4</sub>·nmm] using ω scans. For OsO<sub>4</sub>·nmo (OsO<sub>4</sub>·nmm), 2674 (1301) independent reflections were measured [2θ ≤ 60° (128°)] of which 2242 (1167) had |*F<sub>o</sub>*| > 4σ(|*F<sub>o</sub>*|) and were considered to be observed. The data were corrected for Lorentz and polarisation factors, and semiempirical absorption corrections (based on ψ scans) were applied; the maximum and minimum transmission factors were 0.08 and 0.03 for OsO<sub>4</sub>·nmo and 0.70 and 0.19 for OsO<sub>4</sub>·nmm, respectively.

**Structure analysis and refinement.** The structures were solved by direct methods. The equatorial oxygen atoms in OsO<sub>4</sub>·nmo were found to exhibit a slight rotational disorder; two partial occupancy (55:45) orientations were identified of which the major occupancy atoms were refined anisotropically and the minor occupancy atoms isotropically. The remaining non-hydrogen atoms in OsO<sub>4</sub>·nmo and all of the non-hydrogen atoms in OsO<sub>4</sub>·nmm were refined anisotropically. The positions of the C–H hydrogen atoms in both complexes were idealised, assigned isotropic thermal parameters, *U*(H) = 1.2*U<sub>eq</sub>*(C) [*U*(H) = 1.5*U<sub>eq</sub>*(C of Me)], and allowed to ride on their parent carbon atoms. Refinements were by full-matrix least squares based on *F*<sup>2</sup> to give *R*1 = 0.045 (0.037), *wR*2 = 0.113 (0.104) ‡ for the observed data and 132 (110) parameters for OsO<sub>4</sub>·nmo (OsO<sub>4</sub>·nmm) respectively. The maximum and minimum residual electron densities in the final Δ*F* map were 2.28 (1.54) and –3.01

(–1.35) e Å<sup>-3</sup> respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.000 (0.000) and 0.002 (0.001) respectively. For both structures, computations were carried out using the SHELXTL PC program system.<sup>41</sup>

CCDC reference number 186/590.

### General

Osmium tetroxide was provided by Johnson Matthey plc; all other reagents were obtained from Aldrich and BDH and used without further purification.

### Syntheses

**OsO<sub>4</sub>·nmo.** Osmium tetroxide (0.1 g, 0.39 mmol) was dissolved in dichloromethane (15 cm<sup>3</sup>) and *N*-methylmorpholine *N*-oxide (0.06 g, 0.5 mmol) was added followed by hexane (1 cm<sup>3</sup>). The solution instantly became yellow and the volume was reduced *in vacuo* to *ca.* 2 cm<sup>3</sup>. Upon cooling to –20 °C for 2 h orange crystals formed (Found: C, 16.9; N, 3.8; H, 2.9. Calc. for C<sub>5</sub>H<sub>11</sub>NO<sub>6</sub>Os: C, 16.2; N, 3.8; H, 3.0%). IR spectrum for solution in CH<sub>2</sub>Cl<sub>2</sub> in the ν(OsO) region: 955s and 920 (br) cm<sup>-1</sup>.

**OsO<sub>4</sub>·nmm.** Osmium tetroxide (0.1 g, 0.39 mmol) was dissolved in diethyl ether (15 cm<sup>3</sup>) and *N*-methylmorpholine *N*-oxide (0.06 g, 0.5 mmol) was added followed by hexane (1 cm<sup>3</sup>). The solution instantly became orange and the volume was reduced *in vacuo* to *ca.* 2 cm<sup>3</sup>. Upon cooling to –20 °C for 1 h red crystals formed (Found: C, 17.0; N, 3.9; H, 2.9. Calc. for C<sub>5</sub>H<sub>11</sub>NO<sub>5</sub>Os: C, 16.9; N, 3.9; H, 3.1%). IR spectrum for solution in CH<sub>2</sub>Cl<sub>2</sub> in the ν(OsO) region: 955s and 920 (br) cm<sup>-1</sup>.

***cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> solutions.** To a 1 M aqueous NaOH solution (50 cm<sup>3</sup>) OsO<sub>4</sub> (0.02 g, 0.08 mmol) was added. After stirring for 15 min at room temperature the orange colour of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> was produced. Electronic spectrum [λ<sub>max</sub>/nm (ε/M<sup>-1</sup> cm<sup>-1</sup>)] 380 (1346), 324 (2300) and 255 (1634). Raman spectrum for a 0.6 M solution of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> in 1 M NaOH in the ν(OsO) region: 915vs and 880m cm<sup>-1</sup>; in the Raman spectrum of solid *cis*-Cs<sub>2</sub>[OsO<sub>4</sub>(OH)<sub>2</sub>] these bands appear at 913vs and at 853m cm<sup>-1</sup>.

***cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> co-oxidant {with [Fe(CN)<sub>6</sub>]<sup>3-</sup>, BrO<sub>3</sub><sup>-</sup> or S<sub>2</sub>O<sub>8</sub><sup>2-</sup>}. To a 1 M NaOH solution (50 cm<sup>3</sup>) containing (a) [Fe(CN)<sub>6</sub>]<sup>3-</sup> (9.9 g, 30 mmol), (b) BrO<sub>3</sub><sup>-</sup> (1.5 g, 10 mmol) or (c) S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (2.7 g, 10 mmol), OsO<sub>4</sub> (0.02 g, 0.08 mmol) was added. After stirring for 15 min at room temperature the orange colour of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup> was produced. The electronic spectrum could not be measured in the presence of [Fe(CN)<sub>6</sub>]<sup>3-</sup> due to its interference. Electronic spectra: in bromate solution in molar aqueous NaOH [λ<sub>max</sub>/nm (ε/M<sup>-1</sup> cm<sup>-1</sup>)] 380 (1260) and 324 (2470); in persulfate 380 (1011) and 324 (2690); in both bromate and persulfate solutions the 255 nm band is obscured by absorption in the ultraviolet by these co-oxidants.**

### General procedure for oxidation of alcohols

The oxidation of benzyl alcohol by these reagents was typical.

(a) Using *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>-[Fe(CN)<sub>6</sub>]<sup>3-</sup>. To a 1 M NaOH solution (50 cm<sup>3</sup>) containing K<sub>3</sub>[Fe(CN)<sub>6</sub>] (9.9 g, 30 mmol) was added OsO<sub>4</sub> (0.02 g, 0.08 mmol) in water (3 cm<sup>3</sup>). The mixture was stirred for 10 min until all solids dissolved and benzyl alcohol (0.216 g, 2 mmol) was added, with stirring for 3 h at room temperature. The reaction mixture was extracted with diethyl ether (3 × 25 cm<sup>3</sup>) to remove unreacted benzyl alcohol or any benzaldehyde primary oxidation product. The alkaline aqueous layer was acidified with 2 M H<sub>2</sub>SO<sub>4</sub> to pH 2, Na<sub>2</sub>SO<sub>3</sub> (2 g) was added to this layer to remove the osmium, filtered, extracted with diethyl ether (3 × 25 cm<sup>3</sup>) and dried over anhydrous MgSO<sub>4</sub> to yield the acid. Acids were identified by their IR spectra, melting points and in some cases by their <sup>1</sup>H NMR spectra.

‡ *R*1 = Σ||*F<sub>o</sub>*| – |*F<sub>c</sub>*||/Σ|*F<sub>o</sub>*|, *wR*2 = [Σ*w*(*F<sub>o</sub>*<sup>2</sup> – *F<sub>c</sub>*<sup>2</sup>)<sup>2</sup>/Σ*w*(*F<sub>o</sub>*<sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>.

For bromate and persulfate as co-oxidants the same modification of procedures as noted above for alcohol oxidations was followed.

**Large-scale oxidation of benzyl alcohol by *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>-BrO<sub>3</sub><sup>-</sup>.** Benzyl alcohol (5.5 g, 50 mmol) was added to a *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>-BrO<sub>3</sub><sup>-</sup> solution (500 cm<sup>3</sup>) prepared by adding OsO<sub>4</sub> (0.5 g, 2 mmol) to 500 cm<sup>3</sup> of 1 M NaOH containing NaBrO<sub>3</sub> (15 g, 100 mmol). The reaction mixture was stirred for 5 h at room temperature and then extracted with diethyl ether (10 × 25 cm<sup>3</sup>) to remove unreacted benzyl alcohol. The alkaline aqueous layer was acidified with 2 M H<sub>2</sub>SO<sub>4</sub> to pH 2 and Na<sub>2</sub>SO<sub>3</sub> (2 g) was added to this layer to remove the osmium, and also to prevent interference by bromine by-products with the benzoic acid so formed. It was then extracted with diethyl ether (10 × 25 cm<sup>3</sup>) and dried over anhydrous MgSO<sub>4</sub> to yield benzoic acid (5.2 g, 85%).

**General procedure for oxidation of aldehydes using *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>-[Fe(CN)<sub>6</sub>]<sup>3-</sup>.**

The oxidation of benzaldehyde is typical. To a 1 M NaOH solution (50 cm<sup>3</sup>) containing K<sub>3</sub>[Fe(CN)<sub>6</sub>] (9.9 g, 30 mmol) was added OsO<sub>4</sub> (0.02 g, 0.08 mmol) in water (3 cm<sup>3</sup>). The mixture was stirred for 10 min until all solids dissolved and benzaldehyde (0.212 g, 2 mmol) was added with stirring for 3 h. The reaction mixture was extracted with diethyl ether (3 × 25 cm<sup>3</sup>) to remove unreacted benzaldehyde. The alkaline aqueous layer was acidified with 2 M H<sub>2</sub>SO<sub>4</sub> to pH 2, Na<sub>2</sub>SO<sub>3</sub> (2 g) was added to the acidified aqueous layer to remove the osmium, filtered, and the filtrate extracted with diethyl ether (3 × 25 cm<sup>3</sup>) and dried over anhydrous MgSO<sub>4</sub> to yield the acid.

For bromate and persulfate as co-oxidants the same modification of procedures as noted above for alcohol oxidations was followed.

**General procedure for the oxidation of alkyl halides using *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>-[Fe(CN)<sub>6</sub>]<sup>3-</sup>.**

The oxidation of benzyl bromide is typical. To a 1 M NaOH solution (50 cm<sup>3</sup>) containing K<sub>3</sub>[Fe(CN)<sub>6</sub>] (9.9 g, 30 mmol) was added OsO<sub>4</sub> (0.02 g, 0.08 mmol) in water (3 cm<sup>3</sup>). The mixture was stirred for 10 min until all solids had dissolved and benzyl bromide (0.314 g, 2 mmol) was added with stirring, for 3 h. The reaction mixture was extracted with diethyl ether (3 × 25 cm<sup>3</sup>) to remove unreacted benzyl bromide. The alkaline aqueous layer was acidified with 2 M H<sub>2</sub>SO<sub>4</sub> to pH 2, Na<sub>2</sub>SO<sub>3</sub> (2 g) was added to the acidified aqueous layer to remove the osmium, filtered, and the filtrate extracted with diethyl ether (3 × 25 cm<sup>3</sup>) and dried over anhydrous MgSO<sub>4</sub> to yield the acid.

For bromate as co-oxidant the same modification of procedures as noted above for alcohol oxidations was followed.

**Oxidation of alkenes**

The oxidation of styrene was typical (a modification of that reported by Sharpless and co-workers<sup>40</sup>). Osmium tetroxide (0.01 g, 0.04 mmol) was dissolved in 0.1 M KOH (30 cm<sup>3</sup>) and the solution became orange indicating the formation of *cis*-[OsO<sub>4</sub>(OH)<sub>2</sub>]<sup>2-</sup>. Dihydroquinidine 4-chlorobenzoate (0.93 g, 2 mmol), K<sub>3</sub>[Fe(CN)<sub>6</sub>] (3.96 g, 12 mmol) and styrene (0.42 g, 4 mmol) in *tert*-butyl alcohol (30 cm<sup>3</sup>) were added to this solution. The reaction mixture was stirred at room temperature for 24 h after which time it was concentrated to dryness *in vacuo*. The residue was extracted with diethyl ether (3 × 25 cm<sup>3</sup>) and dried over anhydrous MgSO<sub>4</sub>. The ether was removed *in vacuo* to yield a white solid, identified by its melting point and <sup>1</sup>H NMR spectrum.

The same procedure as above but using 1 M in place of 0.1 M base, followed by acidification in the manner described above for oxidation of alcohols, gave benzoic acid.

**Instrumentation**

Infrared spectra were measured on a Perkin-Elmer series 1720 Fourier-transform instrument, Raman spectra on a similar instrument with Nd-YAG laser excitation, electronic spectra on a Perkin-Elmer Lambda 3 instrument and <sup>1</sup>H NMR spectra on a JEOL EX-270 spectrometer. Microanalyses were carried out by the Microanalytical service at Imperial College.

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