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Alkylrhenium oxides as homogeneous epoxidation catalysts: activity, selectivity, stability, deactivation¹

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Abstract

Methyltrioxorhenium (VII) (MTO, 1a) and several congeners 1b and 2a-d of formula R-ReO₃ and R-ReO₃·L, respectively, qualify as olefin epoxidation catalysts of high activity and selectivity. Related alkylrhenium (VI) complexes form efficient catalyst precursors as well, since they get oxidized by H_2O_2 to the same active species $CH_3ReO(O_2)_2 \cdot H_2O(3)$. The present paper presents a comparison of this novel class of catalysts with the performance of known, commonly used catalysts. Catalyst stability has been recorded and deactivation reactions are described. The synthesis and crystal structure (X-ray diffraction) of the (pale pink-coloured) monomeric amino-functionalized complex $O_3Re-CH_2CH_2CH_2N(C_2H_5)_2$ (4A) and its (violet) polymeric form (4B) are reported. Only the latter is an active epoxidation catalyst with H_2O_2 . An improved laboratory method of the standard catalyst MTO 1a is described.

Key words: catalysis; olefins; oxidation; rhenium

1. Introduction

Up to now, rhenium has not played any role in the oxidation of olefins, be it in stoichiometric or in catalytic reactions [1]. The few reports devoted to this topic unfold a remarkable failure of simple inorganic rhenium compounds to catalyze any specific type of oxidation [2a,b]. This observation is all the more surprising as rhenium's neighbours in the periodic table – tungsten and osmium, respectively – form olefin oxidation catalysts of outstanding activity and selectivity: while tungsten oxide WO₃ behaves as an efficient epoxidation catalyst, osmium tetraoxide OsO₄ is a well-known *cis*-hydroxylation catalyst

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[1a-c,3-5]. No straightforward explanation is available as yet to account for these fundamental mechanistic differences.

The picture changed when reports appeared in the literature, according to which the structurally well-defined methyltrioxorhenium(VII) (MTO, 1a) [6] represents a rhenium catalyst to selectively epoxidize olefins at high catalytic turnovers at room temperature and even below [7]. A key patent has been granted to this finding [8]. In contrast to several metal-containing epoxidation catalysts (e.g., $[O=V(O_2)_2]^-$), no decomposition of H_2O_2 is effected by CH_3ReO_3 (and the active species $CH_3ReO(O_2)_2 \cdot H_2O$, 3). The present paper is to compare the catalytic behavior of MTO and several congeners in olefin epoxidation with related, commonly used catalysts.



2. Results and discussion

For the sake of comparison, a short list of catalysts for olefin oxidation (epoxidation and *cis*-hydroxylation) is given in Table 1 [9]. It can be seen from these data that MTO is one of the few oxidation catalysts that perform well enough around temperatures at and below ambient. Among the epoxidation catalysts, only Groves' manganese/porphyrin systems [9a,10] can successfully compete with MTO in terms of yields and turnover numbers (TON). cis-Hydroxylation mediated by osmium tetraoxide is also an efficient, catalytic reaction. However, it is not a subject of comparison since OsO₄ is a singular case [4a,11]. A rhenium (V) porphyrin complex recently patented by Buchler et al. is to be mentioned (Table 1), albeit higher temperatures (typically 70° C) are required; at the same time, lower product yields result [9b]. Finally, Warwel et al. showed that dirhenium heptaoxide Re_2O_7 , a most simple compound, is a catalyst for olefin epoxidation with subsequent ring-opening to give 1,2diols (trans-configuration) [2b]. However, these reactions only work at high temperatures and high concentrations of the primary oxidant hydrogen peroxide, with typical conditions being 90° C, 60% H₂O₂, 16 h. Furthermore, only 1,4-dioxane as a solvent seems to work [2b], and unwanted side reactions occur.

A few other rhenium compounds [12] that catalyze the oxidation of olefins to *trans*-glycols are shown in Table 2. With the single exception of MTO, however, those are completely inactive at room temperature, even at reaction times of several days. Beyond that, all simple inorganic rhenium compounds (oxides, salts) and most other checked organorhenium compounds are not effective.

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Selected organometallic ar	id coordination compounds th	iat catalyse olefin epoxidatioi	n and hydroxyla	tion			
Compound	Oxidant	Olefin	T (°C)	t (h)	TON	Yield (%)	Ref.
Epoxidation CH ₃ ReO ₃	H " 0, (5%)	cyclooctene	15	16	1000	66	this paper
5	$H_{2}O_{2}(5\%)$	cyclohexene	10	3	450	95	1
	$H_{2}O_{2}(5\%)$	carvon	õ	18	250	85	
$Cp^{*}(CH_{3})Re(=0)CI$	$H_2O_2(10\%)$	cyclohexene	06	2	100	68 ^b	
Re ₂ O,	$H_{2}O_{2}(60\%)$	cyclohexene	06	16	50	74 ^b	2b
TPP[Re(CO) ₃] ₂ ^e	$H_2O_2(85\%)$	cyclooctene	40	10	310	58	9a
ORe (TTP) OCH3d	$H_{2}O_{2}(85\%)$	cyclohexene	60	9	300	68	9b
Cn [*] MnO.Cl*	(CH_),COOH	cvclonctana	60	Þ	40	80	00

CH ₃ ReO ₃	$H_{2}O_{2}$ (5%)	cyclooctene	15	16	1000	66	this _l
	H_2O_2 (5%)	cyclohexene	10	e	450	95	
	$H_{2}O_{2}(5\%)$	carvon	5 C	18	250	85	
$Cp^{*}(CH_{a})Re(=0)CI$	H ₃ O ₂ (10%)	cyclohexene	6	2	100	68 ^b	
Re,0,	H ₂ O ₂ (60%)	cyclohexene	60	16	50	74 ^b	2b
TPP[Re(CO) ₃] ₂ ⁶	$H_{2}O_{2}(85\%)$	cyclooctene	40	10	310	58	9а
ORe(TTP)OCH ₃ ^d	$H_2O_2(85\%)$	cyclohexene	60	9	300	68	96
Cp [*] MoO ₂ Cl [•]	(CH ₃) ₃ COOH	cyclooctene	60	4	40	80	9c
(NH4) ₆ [Mo ₇ O ₂₄]	H_2O_2 (30%)	cyclooctene	40	24	75	12	96
MoO ₂ (HDP) ^f	(CH _a) ₃ COOH	cyclohexene	40	5	100	I	9e
$MoO_2(acac)/N-methylprolinol$	cumene hydroperoxide (80%)	3-methyl-2-butene-1-ol	60	6	100	65	J6
[Mn(AcphpnOH)]Cl·H ₂ O [*]	PhIO	cyclooctene	25	ı	70	28	9g
Mn(Cl ₁₂ TMP)Cl ^b	KHSO ^{5¹}	cyclooctene	25	1	800	65	ЧG
RuCl ₃	PhIO	cyclohexene	20	0.5	20	11	9i
cis-Hydroxylation							
OsO4	(CH ₃) ₃ COOH	cyclohexene	0	16	310	62 ^k	9k
*TON is defined as the molar rat	tio of product (epoxide or diol) t	to catalyst.					
^b trans-1,2-Cyclohexanediol.							
$^{\circ}\text{TPP} = \text{tetraphenylporphinato}$							
$^{d}T^{T}P = 5,10,15,20$ -tetrakis (p-to	lyl)porphyrin.						
Cp^{*} = pentamethylcyclopentadi	enyl.						
f HDP = 2-hydroxyphenylhydraz	ono-pentane-2,4-dione.						
^z AcphpnOH = Schiff base derive	d from reaction of 2-hydroxyace	tophenone and 1,3-diamin	opropan-2	2-ol.			
$^{\rm b}TMP = tetramesitylporphyrin.$							
¹ KHSO ₆ 100×10 ⁻³ M in 10 ml c	of aqueous phosphate buffer 0.25	M (pH=7).					
^k Yield based on <i>cis</i> -1,2-cyclohex	anediol.						

TABLE 2

Compound	<i>t</i> (h)	Yield ^b (%)	Ref.
CH ₃ ReO ₃	0.08	95 (25°C) °	
Na[ReO4]	16	0	
K[ReO ₄]	16	0	
$NH_4[ReO_4]$	16	0	
$[N(n-C_4H_9)_4][ReO_4]$	16	0	
$[NH_3(t-C_4H_9)][ReO_4]$	16	0	
$(CH_3)_3Sn[OReO_3]$	16	0	6c, 12a, b
(CH ₃) ₃ Si[OReO ₃]	16	0	12 a
ReO ₂	16	0	
ReO ₃	16	0	
Re ₂ O ₇ ^d	18	0 (25°C)	
	18	50 (65°C)	
	1.5	25	
	18	90	
Cp [*] ReO ₃ *	5	0	15a
Cp'ReO ₃ ^f	5	0	12c
CpReO ₃ ^g	5	0	12c
$(\sigma$ -Mesityl)ReO ₃ ^h	5	0	15d
$(\sigma$ -Phenyl)ReO ₃	5	0	15b
$Cp^{T}Re(CO)_{3}$	5	0	12d
$\operatorname{Re}_2(\operatorname{CO})_{10}$	16	0	
Cp [*] ReOCl ₂	1	48	12e
Cp [*] ReOBr ₂	1.5	45	12e
	10	85	
$Cp^{*}(CH_{3})Re(=0)Cl$	2	68	12f
	17	87	
$Cp^{*}(t-C_{4}H_{9}C=)ReCl_{2}$	2	27	12g
$CF_3C(=0)ORe(CO)_5$	1	0	12h
$CF_3CORe(CO)_5$	1	40	12i

Activity of various rhenium compounds in olefin oxidation.⁴ The list of references corresponds to the synthesis of the respective compounds

*Reaction conditions: 0.2 mmol of catalyst, 10 mmol (1 ml) of cyclohexene H_2O_2 (10%) in 1,4-dioxane (5 ml), T=90 °C unless otherwise noted.

^btrans-1,2-Cyclohexanediol.

^cDue to the very high catalyst activity, the reaction mixture starts to boil $(T=100^{\circ}C)$.

 ${}^{d}\text{Re}_{2}\text{O}_{7}$ is also active in THF solution (10% H_{2}O_{2}) at 65 $^{\circ}\text{C}$ (50% yield).

Cp^{}=pentamethylcyclopentadienyl.

^fCp' = methylcyclopentadienyl.

 ${}^{\mathbf{g}}Cp = cyclopentadienyl.$

 $^{h}\sigma$ -Mesityl=2,4,6-trimethylphenyl.

2.1. Epoxidation with the catalyst MTO

It seems that MTO 1a is presently among the most active known olefin oxidation catalysts, cf. Table 1. A major advantage is its activity at room tem-



Fig. 1. Catalytic activity of Re_2O_7 and MTO/2.2'-bipyridine in the oxidation of cyclohexene by H_2O_2 .



Scheme 1.

perature and below. Using cyclohexene as a standard olefin, it can be seen from Fig. 1 that simple Re_2O_7 does not show any activity at 25°C in the presence of 10% hydrogen peroxide. At higher temperatures (70°C), some reasonable activity occurs, but only the subsequent ring-opening product *trans*-1,2-cyclohexanediol is formed under such conditions [2b]. MTO in the presence of 2,2'-bipyridine (molar ratio 1/6) exhibits both high activity and selectivity without any noticeable induction period; only the epoxide is formed at 25°C (Fig. 1).

MTO becomes even more active in the absence of pyridine bases. However, acid-catalyzed ring-opening of the epoxide then *can* occur, depending on the specific epoxide in question. We suggest that perrhenic acid HReO₄ from $\text{Re}_2\text{O}_7-\text{H}_2\text{O}_2$ is responsible in Warwel's system [2b] for the observed extensive epoxide ring-opening. As we showed by check experiments, Re_2O_7 does not improve in terms of selectivity upon addition of pyridine or 2,2'-bipyridine as "co-catalysts"; by way of contrast, the activity is further reduced.

The epoxidation mechanism of CH_3ReO_3/H_2O_2 has been established [13,14]. Albeit numerous organorhenium oxides [15] behave as homogeneous or – after grafting on polymers – heterogeneous catalysts for olefin epoxidation [8], we focus our present discussion on the parent compound methyltrioxorhenium(VII) (MTO, 1a). Further derivatives are listed in Scheme 1. MTO can be employed in epoxidation reactions within a broad range of temperatures, normally $-30^{\circ}C$ to $100^{\circ}C$, typically $10-40^{\circ}C$ [8].

As a pure compound, MTO decomposes even at 300° C in a sealed tube (normal pressure or vacuum) only very slowly [16,17]. In addition, the concentrations of catalyst and oxidant can be varied almost ad lib, which advantage also applies for the choice of solvent, with alcohols such as *tert*-butanol being studied best. Examples are listed in Table 3. We stress that MTO can be employed in high-scale laboratory reactions, cf. Table 3 [8,17] and Experimental.

2.2. Synthesis of the catalyst MTO

Several procedures are available for the preparation of the catalyst MTO. We presently favour the combined synthesis following eqns. (1a) and (1b). The first part refers to a known procedure [6d,16]. The second step, (eqn. (1b)) converts the catalytically as yet useless trimethylstannyl perthenate of eqn. (1a) into MTO by means of trichloroacetic anhydride. The product workup consists of (repeated) sublimation [6e,17b]. Total yields of 80–90%, based on total rhenium, are typical of this strategy. Fully deuterated CD_3ReO_3 , however, is preferentially made from Re_2O_7 and $(n-C_4H_9)_3Sn(CD_3)$ (in acetonitrile at 80°C) for the reason that $Sn(CD_3)_4$ is more expensive than rhenium and only 1/4 of the deuterium is utilized in this latter case.

$$\operatorname{Re}_{2}O_{7} + \operatorname{Sn}(\operatorname{CH}_{3})_{4} \to \operatorname{CH}_{3}\operatorname{Re}O_{3} + (\operatorname{CH}_{3})_{3}\operatorname{SnOReO}_{3}$$
(1a)

$$(CH_{3})_{3}SnOReO_{3} + \begin{pmatrix} Cl_{3}CC\\ O \end{pmatrix}_{2}O + Sn(CH_{3})_{4}$$
$$\xrightarrow{CH_{3}CN}CH_{3}ReO_{3} + Cl_{3}CCOSn(CH_{3})_{3} \qquad (1b)$$

2.3. Catalyst selectivity

Sensitive olefins such as 2,3-dimethyl-2-butene and cyclo-1,4-hexadiene form their acid-sensitive epoxides with high selectivities at temperatures as low as -30 °C. The more electron-rich double bond is expectedly oxidized first. Thus, vinylcyclohexene is attacked at the *endocyclic* double bond before the exocyclic vinylic double bond is subject of oxidation. Epoxidation of carvon

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purity (%) 90, 100 88, 100 40, 93 45, 98 40, 90 99, 99 85, 98 72, 94 75, 92 Yield. 95 87, 85 ĝ 2-mentha-6-en-8,9-epoxy-2-one (76.3) 1,2-dihydroxy-4-vinylcyclohexane rans-1,2-cyclohexanediol (103.3) rans-1,2-cycloheptanediol (19.4) .2,4,5-diepoxycyclohexane (6.0) rans-1,2-cyclopentanediol (9.0) .2-epoxycyclohex-4-ene (4.6) I,2-epoxycyclopentane (8.9) epoxycyclooctane (963) Product (g) 95.1) **(** က 28 2 8 20 62 () 0 30 5 4 5 0 12 ŝ 6 MTO-catalyzed epoxidation of olefins with H_2O_2 in tert-butanol 0.20 (0.8) 1.90 (7.6) 0.13 (0.5) ((lomm)) 0.40(1.6)0.20 (0.8) 0.76 (3.0) 0.54(2.2)MTO ھ 85 (0.54) 88 (0.71) [ml (mol)) 19 (0.22) 100 (0.77) (66.0) 001 20 (0.17) (000 (7.68) 11 (0.12) Amount 1,4-cyclohexadiene 4-vinylcyclohexene cyclopentene cycloheptene cyclohexene cyclooctene carvone Olefin 8 م Ъ e æ 4... ъ

^aIn THF solution.

68, 98 50, 98 40, 93

1,2-epoxy-3,3-dimethylbutane (24.5) 2,3-dimethyl-2,3-epoxybutane (21.0)

l,2-epoxyhexane (51.4) .,2-epoxydecane (49.1)

15 15 15

0.55 (2.2) 0.34 (1.4) 0.30 (1.2) 0.40 (1.6) 73, 96 30, 90

.,2-epoxy-4-perfluorohexylbutane (17.6)

.4-dichloro-2.3-epoxybutane (14.5) 2,3-dimethyl-2,3-butanediol (19.8)

48

15 25

0.30(1.2)0.20 (0.8)

15 (0.14)

46 (0.15)

4-perflourohexyl-1-butene cis-1,4-dichloro-2-butene

8

9

-25

46 (0.36) 50 (0.42)

2,3-dimethyl-2-butene 3,3-dimethyl-1-butene

80 (0.42)

1-hexene 1-decene

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<u>-M</u>

only occurs at the exocyclic olefin. It is not surprising that deactivated olefinic systems such as 1,4-dichloro-2-butene and mesityl oxide are oxidized at lower rates (Table 3).

2.4. Epoxide ring-opening

Hydrolytic ring-opening of the epoxides as the primary product is also catalyzed by the alkylrhenium oxides since $1a-H_2O$ and 3 act as Brønsted acids resulting from the strong Lewis acidity of the heptavalent rhenium in R-ReO₃ [18]. In the context of Table 4, it is noted that the reactive peroxo complex 3 (oxygen transfer, cf. ref. 14) is much more Brønsted acidic than the parent compound MTO [17]. MTO/H₂O₂ shows better selectivity for epoxide ring opening (= $[H^+]$ -catalyzed hydrolysis) than aqueous hydrochloric acid. Furthermore, MTO/H₂O₂ has a higher activity than aqueous H[BF₄] with regard to *trans*-glycol formation from epoxycyclohexane, as shown by the check experiments of Table 4. This corresponds to a catalytic effect originating from the metal center of the catalyst.

It has been mentioned previously [7,13] that the reaction conditions for olefin oxidation largely depends on i) the reactivity of the olefin itself, and ii) the lability of the resulting epoxide for acid-catalyzed ring-opening to the 1,2-diol. If cyclo-olefins are employed, then the *trans*-configuration is observed exclusively in the final 1,2-diol derivatives. For this reason, the acidity of the oxidation solutions must be kept as low as possible. To avoid this secondary reaction, nitrogen bases such as pyridine, 2,2'-bipyridine, quinuclidine, or quinine may be added to such solutions [7,8,13]. A recent patent claims secondary aryl alkyl alcohols to suppress epoxide ring-opening during MTO/H₂O₂-catalyzed epoxidation reactions [19].

TABLE 4

Reagents (mmol)	t (h)	Product	Yield (%)
MTO (0.08), H ₂ O (28) ^a	18.2	trans-1,2-cyclohexanediol	85
MTO (0.08) , H_2O_2 (12), H_2O (28) ^b	0.16	trans-1,2-cyclohexanediol	80
	1.0		98
HCl (8.8), H ₂ O (55)	0.16°	2-chloro-cyclohexanol	27
· · · · - · ·		trans-1,2-cyclohexanediol	2
HCl (18), H ₂ O (55)	0.16°	2-chloro-cyclohexanol	57
		trans-1,2-cyclohexanediol	3
$H[BF_4]$ (8.8), H_2O (55)	0.16	trans-1,2-cyclohexanediol	33
	0.5°		61

MTO- and acid-catalyzed hydrolysis of epoxycyclohexane in tert-butanol (standard reaction: 10 mmol of epoxycyclohexane in 8 ml of tert-butanol at 25° C)

 $^{a}pK_{a}(MTO) = 7.5.$

 ${}^{\rm b}{\rm p}K_{\rm e}({\rm MTO}/{\rm H}_2{\rm O}_2)=3.8.$

^cSame yields after 1 h reaction time.

2.5. CH_3ReO_3 vs. OsO_4

We stress that isoelectronic compounds such as CH_3ReO_3 and OsO_4 behave principally different with regard to their role in olefin oxidation. While CH_3ReO_3 quickly forms a structurally well-defined peroxo complex [14], OsO_4 has long been known to effect *cis*-hydroxylation of olefins via direct cycloaddition, with the primary oxidant not being engaged in this first step of the mechanism [4]. The factors governing these fundamental mechanistic differences are not clear as yet, cf. ref. 11, but should become evident from a study using rhenium oxides of general formula X-ReO₃, with X being substituents of differing (group) electronegativity. Such a study is in progress.

2.6. Base-functionalized derivatives of MTO: synthesis and structural chemistry

The beneficial nitrogen-base effect mentioned above stimulated the synthesis of MTO derivatives that contain a (σ -basic) nitrogen functionality attached to the alkyl group. We succeeded in making the γ -aminoalkyl complex **4A** according to eqn. (2) by treatment of Re₂O₇ with the organozinc precursor Zn[CH₂CH₂CH₂N(C₂H₅)₂]₂ in a solution of tetrahydrofuran (THF).

2 Re₂O₇ + Zn[CH₂CH₂CH₂N(C₂H₅)₂]₂

44

$${}^{H_{2}C} \xrightarrow{CH_{2}}_{0 \in \mathbb{N}} \xrightarrow{N_{2}C_{2}H_{5}}_{C_{2}H_{5}} + Zn(thf)_{2}(ReO_{4})_{2}$$
(2)

The new organorhenium (VII) oxide 4A (yield 93%) is monomeric and contains a chelating γ -diethylamino-*n*-propyl group. We suggest that a similar preparation starting from trichloro- or trifluoroacetyl-perrhenate O₃Re-O-C(=O)CX₃ [6e,20] will prove possible, too. 4A represents air- and water-stable pink-coloured crystals (from THF at -30° C) that melt at 95°C under decomposition (black residue).

The crystal structure of 4A is shown in Figs. 2 and 3. In almost all known compounds of formula R-ReO₃·L (2), the donor ligand L is *trans*-oriented with respect to the alkyl group R (Fig. 4). The geometry of these alkylrhenium(VII) oxides is best described as fairly ideal trigonal bipyramidal with approximate C_{3v} symmetry. By way of contrast, the structure of 4A is not easily described in terms of a regular polyhedron due to the *cis*-orientation of the donor amino-functionality (Fig. 4). The coordination geometry is comparable with that of the aniline 1/1-adduct **2f**-*cis* of MTO **1a** [21]. In both cases, the structures are best described as strongly distorted trigonal bipyramids (C_s symmetry, see Fig. 4).

Within this simplified view, the alkyl group (C1) and the two oxo groups (O1 and O2) take up the *equatorial*, O3 and the amino functionality (N1) the *axial* positions. Due to the envelope conformation of the five-membered ReC_3 N ring system, the entire molecule does not have any element of symmetry. If



Fig. 2. PLATON representation of [3-(N,N-diethylamino)-n-propyl]trioxorhenium(VII) 4A as obtained from a single crystal X-ray diffraction study at -50° C. The thermal ellipsoids are at 50% probability level. Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-76344 Eggenstein-Leopoldshafen 2 (Germany), on quoting the depository number CSD-57766, the names of the authors, and the journal citation. Selected bond lengths (pm) and angles (deg): Re-N1 238.3(3); Re-O1 172.1(3); Re-O2 170.7(3); Re-O3 172.5(3); Re-C1 213.6(4); C1-C2 149.9(6); C2-C3 151.4(5); C3-N1 149.1(4); O1-Re-O2 117.1(1); O2-Re-O3 105.2(2); O1-Re-O3 106.0(2); O1-Re-C1 115.6(1); O2-Re-C1 118.4(1); O3-Re-C1 88.6 (2); N-Re-O1 82.5(1); N-Re-O2 82.2(1); N-Re-O3 163.8(1); Re-N-C3 104.0(2); Re-C1-C2 117.5(2); C1-C2-C3 110.7(3).



Fig. 3. View of the structure of 4A down the chelating *N*,*C*-metallacycle to show the *envelope*-configuration (PLATON representation).

one considers only the core geometry of compounds 4A and 2f-cis, then the axial oxo group, the atom C1, the donor atom (N), and rhenium define a mirror plane. The bis(peroxo) complex 3 of MTO exhibits the same coordination



Fig. 4. Cis- and trans-geometries of alkyltrioxorhenium base adducts.

TABLE 5

Structural comparison of 4A and complexes of type $CH_3ReO_3 \cdot L$ (2b-f)

	Re-C (pm)	Re-N (pm)	
4A	213.6(4)	238.3(3)	
2b (ref. 15c)	210.5(4)	240.7(3)	
2c (ref. 15b)	207(1)	238.7(7)	
2d (ref. 15c)	209.2(4)	243.2(3)	
2e (ref. 15b)	209.7(8)	240.8(6)	
2f-cis (ref. 18a)	211.9(5)	233.3(5)	
2f-trans (ref. 18a)	209.5(5)	246.9(4)	

geometry. In this latter case, a water molecule is *cis*-oriented instead of the amino functionality of compounds 4A and 2f-*cis*, while the two peroxo groups occupy the *equatorial* positions (replacing the two oxo groups of 4A and 2f-*cis*, Fig. 4).

Within the limits of the 3σ deviations, all three Re–O bond distances of 4A are identical, indicating no significant *trans*-influence to arise from the amino functionality. The Re–N1 bond distance recorded at a length of 238.3(3) pm resembles those of the known *trans*-oriented quinuclidine 1/1-adducts of alkyl rhenium oxides (Table 5; d(Re-N) = 238.7(7) - 243.2(3) pm, for R=CH₂CH₃, CH₂CH(CH₃)₂, cyclopropyl, and CH₂C(SiMe₃)₃). The Re–N bond of the *trans*-isomer of the aniline complex CH₃ReO₃(NH₂C₆H₅) (2f-*trans*) is somewhat longer (246.9(4) pm) than in the *cis*-isomer.

The rhenium-to-carbon bond length in 4A (213.6(4) pm) is longer than those recorded for the quinuclidine adducts $R-\text{ReO}_3 \cdot \text{Quin } 2b-e: (207(1)-210.5(4) \text{ pm})$ and for the *trans*- and *cis*-isomer of $\text{CH}_3\text{ReO}_3 \cdot \text{NH}_2\text{C}_6\text{H}_5$ (209.5(5), 211.9(5) pm) [21].

The high structural analogy between 4A and the peroxo complex 3 holds

promise towards the implementation of chirality necessary for enantioselective oxidation by means of this new kind of structurally defined organometal oxide.

Under slightly modified conditions, 4B is isolated in 90% yield in place of 4A. The two compounds have the same empirical formula $C_7H_{16}NO_3Re$. 4B is not soluble in any commonly used organic solvent, just in contrast to the very soluble 4A (e.g., *n*-pentane, toluene, CH_2Cl_2 , etc.). We thus propose 4B to have a *polymeric* constitution which assignment is not in conflict with the infrared data, cf. Experimental. Other connectivities (constitution) including a three-dimensional structure via the nitrogen donor functionalities in addition to oxygen bridging can not be ruled out at the present stage.



More importantly, **4B** easily dissolves in aqueous hydrogen peroxide (*tert*butanol as a solvent) to give a dark-yellow solution. As can be monitored by GC/MS spectroscopy, this compound is once again active and more selective in olefin epoxidation than **1a**, while its monomolecular isomer **4A**, see above, neither reacts with H_2O_2 nor catalyzes olefin epoxidation. Further work is in progress to exploit this strategy and to understand the structural prerequisites of peroxo formation.



Fig. 5. Comparison of the catalytic activities of alkyltrioxorhenium compounds and their quinuclidine derivatives in terms of their oxidation of cyclooctene by H_2O_2 .

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2.7. Influence of alkyl groups

One could have predicted that higher alkyl derivatives of MTO would not qualify in catalysis due to their lower thermal stability [15b,c]. However, a comparative study has shown that, curiously enough, quite a few compounds $R-ReO_3$ become more stable upon treatment with hydrogen peroxide, even in the presence of water. Furthermore, the quinuclidine 1/1 adducts $R-ReO_3 \cdot L$ (L=quinuclidine) can be employed in order to gain thermal stability [15b]. Figure 5 summarizes the results obtained for the oxidation of cyclooctene by means of H_2O_2 at 13°C. It is noteworthy that the cyclopropyl derivative 2c is more active in epoxidation than MTO·Quin 2a. Since these complexes are of comparable thermal stability [15b], both with and without H_2O_2 , an electronic



Fig. 6. Catalytic activity of the organorhenium (VI) oxides **5a** and **5b** in the oxidation of cyclooctene by H_2O_2 as compared to the catalytic activity of MTO.





effect of the cyclopropyl group is the most obvious explanation of this catalytic result. Further work to substantiate this proposal is in progress.

2.8. Re^{VI} vs. Re^{VII}

High activity and selectivity in olefin epoxidation is maintained as long as an alkyl group resides at rhenium (VII). The dinuclear, thermally rather stable, easy-to-make Re^{VI} complexes **5a** and **5b** [6c,15i] show nearly the same catalytic properties as MTO, cf. Fig. 6. While this behaviour is at first sight surprising, an explanation is seen in Scheme 2: the primary oxidant H_2O_2 converts the dinuclear precursor compound via oxidation to MTO, with concomitant elimination of mostly methane and ethane (molar ratio 1/5). These products are likely to be formed along radical pathways. Interestingly, further oxidation products, e.g. methanol, are not formed in significant amounts. The glycolate complexes **6** [22] and **7** [22] once again mirror the catalytic performance of MTO (Scheme 3, Fig. 6). Due to the clean Re^{VI} to Re^{VII} oxidation, no catalytic active sites are lost upon treatment of **5a**,**b** and **6** with H_2O_2 .



Scheme 3.



Fig. 7. Time-dependent UV/Vis spectra ($\lambda = 190-500$ nm) of 1a in H₂O (10% H₂O₂), $c(1a) = 3 \times 10^{-3} \text{ mol } l^{-1}, c(H_2O_2) = 1.3 \times 10^{-1} \text{ mol } l^{-1}, T = 20^{\circ}\text{C}.$



 $k=2.4 \times 10^{-5} \,\mathrm{s}^{-1}$ (calculation is based on a pseudo-unimolecular reaction), $T=20^{\circ} \mathrm{C}$. (Top right) UV/Vis kinetics at $\lambda_{\mathrm{max}} = 364 \,\mathrm{nm}$ of 3 in tertbutanol, $c(3) = 3 \times 10^{-3} \text{ mol } 1^{-1}$, $k = 1.1 \times 10^{-4} \text{ s}^{-1}$, $T = 20^{\circ}\text{C}$. (Bottom left) UV/Vis kinetics at $\lambda_{\text{max}} = 364 \text{ nm of } 1\text{a}$ in H₂O (10% H₂O₂), $c(1a) = 3 \times 10^{-3}$ mol 1^{-1} , $c(H_2O_2) = 1.3 \times 10^{-1}$ mol 1^{-1} , $k = 1.4 \times 10^{-3}$ s⁻¹ (calculation is based on a pseudo-unimolecular reaction), $T = 20^{\circ}$ C. Fig. 8. (Top left) UV/Vis kinetic at $\lambda_{max} = 364$ nm of 1a in tert-butanol (10% H₂O₂), c(1a) = 3×10⁻³ mol 1⁻¹, c(H₂O₂) = 1.3×10⁻¹ mol 1⁻¹, (Bottom right) UV/Vis kinetics at $\lambda_{\max} = 364 \text{ nm of } 3 \text{ in } \text{H}_2\text{O}, c(3) = 3 \times 10^{-3} \text{ mol } \text{l}^{-1}, k = 4.5 \times 10^{-2} \text{ s}^{-1}, T = 20^{\circ}\text{C}.$

2.9. Catalyst deactivation

¹H-NMR and UV/Vis experiments prove that deactivation of the catalyst MTO is not simply accounted for by hydrolysis of the active species according to eqn. 3

$CH_{3}ReO(O_{2})_{2} \cdot H_{2}O \rightarrow CH_{4} + H[ReO_{4}] + O_{2}$ (3)

to yield methane and perrhenic acid. (Dilute solutions of MTO in D_2O decompose at room temperature very slowly and only incompletely to CH_3D and perrhenic acid). Rather autoxidation of the catalyst with formation of methanol (NMR) constitutes the predominant decomposition pathway (eqn. 4).

$$CH_{3}ReO(O_{2})_{2} \cdot H_{2}O \rightarrow CH_{3}OH + H[ReO_{4}] + 1/2O_{2}$$
(4)

No intermediate could be detected, as shown by UV/Vis kinetic experiments, cf. Fig. 7. Similarly, ETO (1b) forms ethanol as shown by NMR spectroscopy. The perrhenic acid has been detected by UV/Vis spectroscopy.

If an excess of H_2O_2 is present in a solution of 1a in *tert*-butanol (catalysis conditions), then the lifetime of the active species 3 is much higher as compared to the lifetime of isolated 3 in the absence of H_2O_2 . In contrast to the high stability of 1a in *tert*-butanol/exc. H_2O_2 , both, the active system (1a/exc. H_2O_2) and of the bis(peroxo)complex 3 are more labile in water. In addition, the isolated active species 3 slowly decomposes upon dissolution in organic solvents (e.g., THF or diethyl ether). The monoperoxo complex $CH_3ReO(O_2)_2$ is first formed, followed by CH_3ReO_3 (1a). At the same time, O_2 must be eliminated but was not detected due to low concentrations, cf. Table 6 and Fig. 8. It can be seen from Table 6 that both MTO and the active species 3 are more stable in *tert*-butanol than in water. While MTO is stable towards strong protic acids, quick decomposition occurs upon addition of $[OH]^-$, with $[ReO_4]^-$ and CH_4 being formed instantaneously [6a]. Thus no catalytic activity is observed after addition of $[OH]^-$ to the system [13].

TABLE 6

Compound	Solvent	$c(H_2O_2) \pmod{l^{-1}l}$	$k (s^{-1})$
1a	(CH ₃) ₃ COH	1.3×10 ⁻¹	2.4×10^{-5}
1a	H ₂ O	1.3×10^{-1}	1.4×10^{-3}
3	(CH ₃) ₃ COH	0	1.1×10^{-4}
3	H ₂ O	0	4.5×10^{-2}

Catalyst deactivation rates^a

 $c(1a) = c(3) = 3 \times 10^{-3} \text{ mol } l^{-1}, T = 20 \,^{\circ}\text{C}, \lambda_{\text{max}} = 364 \text{ nm}.$

3. Conclusion and perspectives

MTO is a molecular, structurally well defined epoxidation catalyst of easy access, good stability, high activity and selectivity. Instantaneous reaction with hydrogen peroxide, due to the pronounced Lewis acidity of MTO, leads to a very reactive intermediate **3** [14] as the key oxygen transfer species. Higher alkyl congeners R-ReO₃ and R-ReO₃·L (L=nitrogen base ligand) also show good epoxidation performance and high selectivity, as long as the alkyl group R is not eliminated. Product selectivity – epoxide vs. 1,2-diol – can be influenced by addition of nitrogen ligands of the bipyridine and quinuclidine type, by introducing an amino group into the group R, or by pH adjustment. Epoxide ring-opening can thus be suppressed. MTO has opened a new class of epoxidation catalysts in that it now provides the chance of tuning reactivity by means of the ligands R. Chiral derivatives are known, and enantioselective oxidation could result eventually.

4. Experimental

Dirhenium heptaoxide was synthesized by direct oxidation of rhenium grains on a 100 g scale by means of absolutely dry oxygen. For simplicity of preparation the apparatus of Fig. 9 was used.

100 g (0.54 mol) of rhenium were placed in an open ceramic crucible in



Fig. 9. Apparatus used for the preparation of Re_2O_7 .

the first third of a slightly inclined quartz tube of 3 cm diameter and 150 cm length (Fig. 9). The system was purged with dry N_2 at 800°C for 1 h. After lowering the temperature to 500°C, the nitrogen flow was stopped. The oxidation of the rhenium was then started by changing the gas from N_2 to O_2 . (Both gases were dried by passing first through molecular sieve 4 Å and then through concentrated sulfuric acid.) A low oxygen flow was controlled with an oil bubbler at the end of the apparatus. Due to the high temperature, the Re_2O_7 sublimes out of the reaction zone. The sublimed product was collected by means of a long spatula into the adapted Schlenk flask (see Fig. 9). The reaction is finished after approx. 2.5 h. Yield: 126 g (97%).

Since MTO has become a commonly used catalyst in many laboratories, we present here an improved synthesis. Yields and simplicity of work-up are the advantages of the following procedure. The solvent THF (pro synthesi) was repeatedly distilled over Na/K alloy. Acetonitrile (pro analysi) was dried over P_2O_5 and then over K_2CO_3 .

4.1. Methyltrioxorhenium(VII) (1a)

1) A solution of Re_2O_7 (5 g, 10.3 mmol) and tetramethyltin (1.6 ml, 11.6 mmol) in 70 ml of dry THF was heated in a 250 ml Schlenk flask at 67°C (reflux) for 4 h. The solvent was subsequently removed in an oil-pump vacuum at 25°C. This step has to care that no MTO is distilled off with the solvent. The desired product was sublimed from the grey-white residue at 60-80°C/ 10^{-3} mmHg onto a cold finger (0°C) as colourless fine crystals. Isolated yield: 2.4 g (93%).

2) The route described above yields stannylperrhenate $(CH_3)_3SnOReO_3$ as the by-product. It constitutes the sublimation residue and is recrystallized form acetonitrile (4.0 g, 94%). This material can be utilized for the preparation of MTO as follows:

A solution of $(CH_3)_3$ SnOReO₃ (4 g, 9.7 mmol) and trichloroacetic anhydride (1.77 ml, 9.7 mmol) in 60 ml of dry acetonitrile was stirred at 25°C for 4 h. Tetramethyltin (1.5 ml, 10.8 mmol) was then added to the pale-green solution which was then stirred over night at 25°C. The solvent was then carefully removed in an oil-pump vacuum at 25°C. The crude product was consecutively sublimed at 90–100°C/10⁻³ mmHg on to a cold finger (0°C), thus resulting in dark-red crystals. The sublimed material was stirred over night in *n*-pentane. The then yellow solution containing the by-products was separated by filtration through a syringe. The white residue was washed with cold *n*pentane (0°C) and was sublimed once again, as described above. This procedure was repeated twice to finally yield 2.00 g (83%) of pure MTO 1a.

The total yield of MTO, based upon rhenium, amounts to 86% from the combined steps 1) and 2). A scale-up of this procedure to synthesize 25 g (0.10 mol) of MTO in one run is possible by using appropriate sizes of Schlenk and sublimation flasks.

The CD₃ derivative CD₃ReO₃ is synthesized from Re₂O₇ and $(n-C_4H_9)_3$ Sn-CD₃ in dry acetonitrile (80% yield). The details of this preparation will be described elsewhere [17].

4.2. Activity tests of rhenium compounds related to Table 2

4.2.1. General procedure

0.2 mmol (calc. on Re) of the respective catalyst were dissolved in 5 ml of 1,4-dioxane containing 10% H_2O_2 . 10 mmol (1 ml) of pure, distilled cyclohexene were added. Unless otherwise noted, the reaction mixture was stirred for 16 h at 90°C. The yields of products were determined by GC/MS spectroscopy (HP 5890/HP 5970 B; fused-silica capillary column HP-1, 12 m); cycloheptanone was used as an internal standard.

4.3. MTO-catalyzed oxidation of olefins related to Table 3

4.3.1. Oxidation solution

tert-Butanol or THF (1 l) were kept at 25–30 °C and mixed with 0.3 l of perhydrol (or better 0.1 l of 85% concentrated H_2O_2 in order to avoid high amounts of water). The solution was stirred with anhydrous MgSO₄ (250 g or 30 g), for 3 h and then filtered, $c(H_2O_2) = 3 \text{ mol } l^{-1}$. The concentration of the H_2O_2 can be varied almost ad lib but ranges normally between 5–25% (1.2–6 molar solutions).

4.3.2. Catalytic olefin oxidation

MTO 1a (0.13–1.9 g, 0.5–7.6 mmol) was dissolved in the above oxidation solution (50 ml to 3 l, 0.15–9 mol of H_2O_2). The olefin to be oxidized (0.12– 7.70 mol) was added to this yellow catalyst solution, which was either cooled by means of a cryostate (-25 to 10°C) or water (15°C) or was allowed to react at room temperature. In the latter case the reaction mixture can reach the boiling point of the solvents (65 and 80°C, respectively) due to the heat of reaction. For better control, the oxidations were monitored by GC/MS spectroscopy, see above. At the end of the reaction, which in most cases is indicated by decoloration of the solution, any remaining H_2O_2 was decomposed with a mixture of a catalytic amount of MnO_2 and a stoichiometric amount of anhydrous MgSO₄ to remove the resulting water. The suspension was then filtered through a glass frit covered with Celite[®]. The filtrate was than evaporated, the residue – either a liquid or a viscous or solid mass – was distilled or washed with, or recrystallized from common organic solvents (acetone, ethanol, etc.).

4.4. High-scale oxidation of cis-cyclooctene

MTO 1a (1.9 g, 7.60 mmol) was dissolved in 1.5 l of oxidation solution equal to 9 mol of H_2O_2 (c(H_2O_2) = 6 mol l^{-1}). *cis*-cyclooctene (1 l, 7.68 mol) was added dropwise to this yellow catalyst solution (molar ratio H_2O_2/cis cyclooctene/MTO=1184/1011/1). The reaction mixture was then stirred for 24 h at 15 °C. After adding a catalytic amount of MnO₂ and 200 g of anhydrous MgSO₄, the grey suspension was filtered through a glass frit coated with Celite[®]. The solvent was removed from the colorless filtrate under vacuum (oil pump). The crude, colorless product showed a purity of 99% without any further purification (mp. 53-55°C).

4.5. Hydrolysis of epoxycyclohexane related to Table 4

Epoxycyclohexane (10 mmol) was dissolved in *tert*-butanol (8 ml). After adding MTO/H₂O, MTO/H₂O₂/H₂O, HCl_{aq}, or HBF_{4(aq)} (amounts noted in Table 4), the reaction mixtures were stirred at 25 °C. Yields of the products were determined by GC/MS after 0.16, 0.5, 1, and 18 h (internal standard: cycloheptanone).

4.6. Kinetics of the alkylrhenium oxide catalyzed oxidation of cis-cyclooctene

4.6.1. General procedure

0.12 mmol (calc. on Re) of the various catalysts (Fig. 5) were dissolved in 5 ml of oxidation solution (15 mmol H_2O_2). To the chilled solution (13°C), 1.5 ml (11.5 mmol) of *cis*-cyclooctene were added. The reaction was monitored by GC/MS spectroscopy (internal standard: cycloheptancne).

4.7. Synthesis of [3-(N,N-diethylamino)-n-propyl]trioxorhenium(VII)(4)

4.7.1. Isomer 4A

A solution of bis [3 - (N, N-diethylamino) - n-propyl]zinc (0.44 g, 1.5 mmol)[23] in 5 ml of THF was added at -78 °C dropwise to a solution of dirhenium heptoxide (1.5 g, 3.10 mmol) in 30 ml of THF. The mixture was stirred for 1 h at -78 °C and was subsequently warmed up to 0 °C within an hour. To separate the formed zinc perrhenate Zn (THF)₂[ReO₄]₂, the mixture was cooled to -20 °C. The red-brownish solution was then concentrated to 5 ml and was further cooled to -30 °C to isolate analytically pure [3 - (N, N-diethylamino) - n-propyl]trioxorhenium (VII) 4A as pale-pink crystals. 4A should be stored at -30 °C under nitrogen. Yield: 970 mg (90%).

Elemental analysis: Calcd. for C₇H₁₆NO₃Re: C, 24.13; H, 4.63; N, 4.02; Re, 53.44; O, 13.78; Found: C, 24.16; H, 4,62; N, 3.99; Re, 53.42; O, 14.22.

Spectroscopic data: IR [KBr, cm⁻¹]: ν (Re-C) 548 (s); γ (CH) 734 (m); CH₂-rocking 788 (m); ν (Re=O) 916 (vs), 958 (vs), 980 (m); δ_s (CH₃) 1358; ν (C-N) 1381 (m), 1394 (m); δ_{as} (CH₃, CH₂) 1438 (m), 1463 (m), 1475 (m); ν (CH₂) 2881 (s), 2896 (s), 2943 (s), 2958 (s); ν_s (CH₃) 2981 (s); ν_{deg} (CH₃) 3012. ¹H-NMR [d₈-THF, 400 MHz, 25°C, ppm]: δ (CH₃) 1.10 [t, 6H, ²J(H,H)=7.32 Hz]; δ (CH₂) 2.45 [m, 2H]; δ (ReCH₂) 2.70 [t, 2H, ²J(H,H)=6.72]; δ (NCH₂) 2.87 [m, 2H]; δ (NCH₂) 3.48 [m, 4H]. ¹³C{¹H}-NMR [d₈-THF, 100.54 MHz, 25°C, ppm]: δ (CH₃) 8.17; δ (ReCH₂) 23.75; δ (ReCH₂CH₂) 47.24; δ (NCH₂CH₃) 57.42; δ (CH₂N) 73.76. Mass spectra, electron impact at 70 eV, *m/z*, ¹⁸⁷Re, correct isotope pattern: 349 (M⁺⁺); 334 (M-CH₃), 86 (C₅H₁₂N⁺⁺, base peak).

4.7.2. Isomer **4B**

The resulting red-brownish solution – see above preparation – was evaporated to dryness in oil-pump vacuo at -20° C to yield a dark purple, solid residue. **4B** should be stored at -30° C under nitrogen. Yield: 940 mg (87%). Elemental analysis: Calcd. for C₇H₁₆NO₃Re: C, 24.13; H, 4.63; N, 4.02; Re, 53.44; Found: C, 23.49; H, 4.60; N, 3.85; Re, 53.66.

Spectroscopic data: IR [THF, cm⁻¹]: ν (Re=O) 909 (s), 946 (s); ν (CH₂) 2944. ¹H-NMR [d₈-THF, 400 MHz, 25°C, ppm]: δ (CH₃) 1.33 [t, 6H, ²J(H,H)=7.32 Hz]; δ (CH₂) 2.46 [m, 2H]; δ (ReCH₂) 2.94 [t, 2H, ²J(H,H)=7.32 Hz]; δ (NCH₂) 3.12 [m, 2H]; δ (NCH₂) 3.26 [m, 4H].

4.8. UV/Vis spectroscopy

The kinetic investigations were performed with an Hewlett-Packard 8542-A instrument. Data for decomposition studies were obtained from freshly prepared solutions of MTO **1a** (56 mg, 0.22 mmol) in 5 ml of *tert*-butanol (10% H_2O_2) and in 5 ml of H_2O (10% H_2O_2), respectively. To achieve convenient concentrations, 0.2 ml of the yellow-colored solutions were added to 2.8 ml of *tert*-butanol (or 2.8 ml of H_2O , Table 6) and were transferred into the spectrometer (l=1 cm, slit s=2 nm). The calculation of the rate constants is based on the absorbance decrease at $\lambda_{max} = 364$ nm.

4.9. X-ray crystallographic structure of **4A**

 $a=1142.9(2), b=752.7(1), c=1160.6(2) \text{ pm}, \beta=95.126(7)^{\circ}, V=994\times10^{6}$ pm³, measurement at -50 °C, $\rho_{calc} = 2.33$ g cm⁻³, $\mu = 123.6$ cm⁻¹, F(000) = 656, Z=4, monoclinic crystal system, space group $P2_1/c$ (No. 14), Enraf-Nonius CAD4, $\lambda = 71.07 \text{ pm}$ (Mo_{Ka}, graphite monochromator), range of measurement $2.0^{\circ} < \Theta < 25^{\circ}, \omega$ -scan, scan width $(1.5 + 0.3 \tan \Theta)^{\circ} (\pm 25\%)$ before and after each reflection to determine the background, $t_{max} = 75$ s, 3778 measured reflections $(\pm h,k,\pm l)$, 1721 independent reflections of which 1537 had $I > 3\sigma(I)$, structure determination with Patterson methods and difference Fourier syntheses, empirical absorption correction based on Ψ -scan data, transmission coefficients 0.474-0.998, 173 least squares parameters, all 12 heavy atoms with anisotropic thermal parameters, all hydrogen atoms found and independently refined (isotropic), anomalous dispersions [24] accounted for, shift/ $R = \text{sum}(||F_{\rm o}| - |F_{\rm c}||)/\text{sum}|F_{\rm o}| = 0.020,$ $R_{\rm w} = [\rm{sum}$ < 0.0001, error $w(|F_{o}| - |F_{c}|)^{2}/\text{sum}|F_{o}|^{2}]^{1/2} = 0.021$, residual electron density $+1.05 \Delta e/\dot{A}^{-3}$

(87 pm beside Re)/ $-1.06 \Delta e/Å^{-3}$, weighting scheme of Tukey and Prince [25] with three refined parameters P(1) = 1.628, P(2) = -0.273, P(3) = 1.410. All calculations were performed on a DECstation 5000/25 using the programs *CRYSTALS* [26] and *PLATON* [27].

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