



ELSEVIER

Journal of Molecular Catalysis A: Chemical 114 (1996) 169–180

JOURNAL OF  
MOLECULAR  
CATALYSIS  
A: CHEMICAL

# A new dinuclear rhodium(III) ‘sandwich’ polyoxometalate, $[(WZnRh_2)(ZnW_9O_{34})_2]^{10-}$ . Synthesis, characterization and catalytic activity

Ronny Neumann<sup>\*</sup>, Alexander M. Khenkin

*Casali Institute of Applied Chemistry, Graduate School of Applied Science, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel*

## Abstract

The rhodium containing polyoxometalate,  $[(WZnRh_2)(ZnW_9O_{34})_2]^{10-}$  was prepared by reaction of  $[(WZn_3)(ZnW_9O_{34})_2]^{12-}$  with  $RhCl_3$ . The X-ray diffraction showed this compound to be isostructural to other compounds of this series. This was confirmed by the IR spectra. The elementary analysis and cyclic voltammetry measurements indicated that the polyoxometalate was of high purity. Epoxidation of alkenes with 30% aqueous  $H_2O_2$  in 1,2-dichloroethane/water biphasic systems using  $[(WZnRh_2)(ZnW_9O_{34})_2]^{10-}$  as catalyst showed high overall activity as compared to other noble metal substituted polyoxometalates of this series. The reactions were highly selective to epoxidation of cyclohexene and similar to previously reported  $[(WZnMn_2)(ZnW_9O_{34})_2]^{12-}$ , except that hydrogen peroxide yields were measurably higher in the rhodium case. The  $[(WZnRh_2)(ZnW_9O_{34})_2]^{10-}$  catalyst appears to be stable under turnovers conditions. Using IR spectroscopy as a probe to compare active polyoxometalates (Rh and Mn) versus an inactive one (Zn), showed that in the former case peroxy-tungstate intermediates could be identified whereas for the inactive compound no such intermediate was observed. A possible mechanism taking into account reactivity, steric constraints and IR spectra assuming structural integrity under catalytic turnover conditions was put forth.

*Keywords:* Rhodium polyoxometalate; Hydrogen peroxide activation; Epoxidation

## 1. Introduction

Pre-1983 interest in the field of heteropolyanion or polyoxometalate chemistry was thoroughly summarized in Pope's book [1]. Since the publication of this monograph, there has been a significant and much increased research interest in polyoxometalate chemistry. This research has been described in several reviews dealing with different aspects of this chemistry

including general overviews [2], structure [3], photochemistry, photocatalysis [4], and catalysis [5]. Heteropolyoxometalate compounds where either the heteroatom or more usually one or perhaps more of the addenda are substituted by lower valent transition metals are called transition metal substituted polyoxometalates, TM-SPs. These compounds are uniquely synthetically attractive as well as interesting as oxidation catalysts because one may visualize these compounds as having reactive low valent transition metal centers complexed by inorganic oxometalate ligands which have high capacity for

<sup>\*</sup> Corresponding author.

electrons. In addition, the exclusively inorganic nature and the high valent  $d^0$  state of the polyoxometalate ‘ligands’ makes them inherently stable towards decomposition under oxidation conditions as well as themselves having interesting potential catalytic properties. Both the stability and potential activity at the transition metal site and polyoxometalate ‘ligand’ is crucial to their future development and industrial application in catalytic oxidations especially for fine chemicals [6].

The most common class of transition metal substituted heteropolyoxometalates are those that are based on the mono-substituted Keggin and Wells–Dawson structures. Synthesis and characterization of transition metal substituted heteropolyoxometalates with lower valent transition metals such as cobalt, manganese, copper, iron, or even cerium among others as the *heteroatom* is well known in the literature [7], but they have received relatively little attention as catalysts [8] because of the inaccessibility of the transition metal to coordination by a substrate. On the other hand, *addenda* substituted compounds although first prepared from lacunary heteropolyoxometalates (almost always polyoxotungstates due to the lower stability of the polyoxomolybdates) over twenty years ago [9], e.g.  $[\text{SiCo}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ , have only in the past decade been shown to have interesting coordination chemistry. For example, in these systems, ligands such as dioxygen may be ligated to manganese [10], high valent chromium–oxo compounds are formed with oxygen donors [11] and ruthenium centers have been shown to coordinate various substrates [12]. The catalytic use of these compounds has been realized in a few cases such as in the epoxidation of alkenes by iodosobenzene with addenda substituted Keggin [13] and Dawson [14] compounds and the hydroxylation of alkanes by *tert*-butylhydroperoxide [15]. Dioxygen has been used for the oxidation of olefins with aldehydes [16] and other reducing agents [17], and for the oxidation of alkanes [18], sulfides [19] and hindered phenols [20]. The oxidation of alkanes and alkenes

with various other oxidants has also been reported [21]. Transition metal substituted molybdates [22] have been shown recently to be effective as bifunctional catalysts for the one pot autoxidation of alkanes and epoxidation of alkenes with molecular oxygen.

Another subclass of TMSPs, i.e. the di- and tetra-substituted transition metal heteropolyoxometalates pictured as having a ‘ring’ of transition metals ‘sandwiched’ between  $\text{B-XW}_9\text{O}_{34}^{9-}$  [23,24] and  $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$  units [25], have been prepared. Thus,  $[\text{Fe}^{\text{II}}(\text{PW}_9\text{O}_{34})_2]^{10-}$  and  $[\text{WZnMn}^{\text{II}}(\text{ZnW}_9\text{O}_{34})_2]^{12-}$  have been shown to activate  $\text{H}_2\text{O}_2$  for alkene epoxidation [26]. Especially interesting in the context of this paper are the newly synthesized noble metals, Pd(II), Pt(II) and Ru(III), compounds,  $[\text{WZnNM}_2(\text{ZnW}_9\text{O}_{34})_2]^{q-}$  (NM = Pd(II), Pt(II) and Ru(III)) which were also shown to have significant activity in alkene and alkane oxidation [27]; the ruthenium analog is active in the highly selective oxidation of adamantane at the tertiary position with molecular oxygen [28]. Concerning rhodium substituted polyoxometalates, there is as yet just a single literature reference where rhodium has been inserted in Keggin and Dawson structures [29]. Therefore, in this paper we extend our research to the preparation and characterization of the rhodium substituted ‘sandwich’ type polyoxometalate,  $[(\text{WZnRh}^{\text{II}})(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ . Both the physical and oxidative catalytic properties using aqueous hydrogen peroxide as oxidant were investigated. A mechanism for hydrogen peroxide activation has been put forth based on relative reactivities of substrates, the polyoxometalate structure and IR measurements.

## 2. Results and discussion

### 2.1. Synthesis of $[(\text{WZnRh}^{\text{II}})(\text{ZnW}_9\text{O}_{34})_2]^{10-}$

The synthesis of this polyanion was carried out by substitution of the two terminal and more labile zinc atoms in the parent

$[(\text{WZn}_3)(\text{ZnW}_9\text{O}_{34})_2]^{12-}$  polyoxometalate by two rhodium(III) cations in a procedure similar to those described in the past [23,27]. Thus, upon mixing a hot aqueous solution containing 2.5 equivalents of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and one equivalent of  $\text{Na}_{12}(\text{WZn}_3)(\text{ZnW}_9\text{O}_{34})_2$  for 4 h, a color change from deep brown to light brown was observed. After addition of KCl and cooling a light brown solid was precipitated. The crude polyoxometalate was then purified by recrystallization from water with overall yield of 27%. Elementary analysis was consistent with a compound of the formula  $\text{K}_{10}(\text{WZnRh}_2^{\text{III}})(\text{ZnW}_9\text{O}_{34})_2 \cdot 40\text{H}_2\text{O}$ .

## 2.2. Crystal and molecular structure of anion

The rhodium polyoxoanion gave red-brown single crystals for X-ray diffraction as the sodium salt. High quality crystals were obtained by slow evaporation of a solution of the potassium salt in concentrated aqueous sodium nitrate. The structure of the sodium salt,  $\text{Na}_{10}(\text{WZn}(\text{Rh}^{\text{III}}\text{H}_2\text{O})_2)(\text{ZnW}_9\text{O}_{34})_2 \cdot 42\text{H}_2\text{O}$ , Fig. 1, was determined by X-ray crystallography. The crystallographic data, fractional atomic coordinates and selected atomic distances for the central transition metal substituted ‘ring’ are given in Tables 1 and 2 and Fig. 2, respectively. The data show that  $\text{Na}_{10}(\text{WZn}(\text{Rh}^{\text{III}}\text{H}_2\text{O})_2)(\text{ZnW}_9\text{O}_{34})_2 \cdot 42\text{H}_2\text{O}$  is isostructural with other similar transition metal substituted compounds reported and used previously [23,27]. Thus, the rhodium polyoxometalate contains two  $\text{B}-(\text{ZnW}_9\text{O}_{34})^{12-}$  fragments of the Keggin-type polyanion  $[\text{ZnW}_{12}\text{O}_{40}]^{6-}$ . These two fragments are linked through four W, Rh, Zn, Rh octahedrally coordinated metal atoms. The two rhodium atoms are found on the opposite sites of the ‘sandwiched’ rhombus and have five surrounding oxygens belonging to  $[\text{ZnW}_9\text{O}_{34}]^{12-}$  units and a sixth aqua ligand. The interatomic distance between two rhodium atoms is approximately 5.2 Å precluding magnetic interaction between the rhodium centers [27].

## 2.3. Physical properties

The IR spectrum of  $\text{K}_{10}(\text{WZnRh}_2^{\text{III}})(\text{ZnW}_9\text{O}_{34})_2 \cdot 40\text{H}_2\text{O}$  in a KBr pellet shows practically identical features to those of other noble metal substituted analogs [27] with the following features: W–O (terminal)  $926\text{ cm}^{-1}$ ; W–O–W (corner-sharing  $\text{WO}_6$  octahedra)  $879\text{ cm}^{-1}$  and W–O–W (edge-sharing octahedra)  $772\text{ cm}^{-1}$ . The UV-vis spectrum of  $\text{K}_{10}(\text{WZnRh}_2^{\text{III}})(\text{ZnW}_9\text{O}_{34})_2 \cdot 40\text{H}_2\text{O}$  in water, Fig. 3, shows the common polyoxometalate absorption at 306 nm ( $\epsilon = 24,500\text{ M}^{-1}\text{ cm}^{-1}$ ) attributable to W–O–W charge transfer bands. In addition, a peak at 452 nm ( $\epsilon = 1880\text{ M}^{-1}\text{ cm}^{-1}$ ) is observable due to O → Rh charge transfer and/or d–d transitions. A similar absorption band has been observed in the rhodium-substituted Keggin compounds but not in the Wells–Dawson compounds [29].

The cyclic voltammetry of  $\text{K}_{10}(\text{WZnRh}_2^{\text{III}})(\text{ZnW}_9\text{O}_{34})_2 \cdot 40\text{H}_2\text{O}$ , Fig. 4a, was clean indicating that the rhodium polyoxometalate was of high purity. At a low negative potential a quasi-reversible wave at  $E_{1/2} = -0.28\text{ V}$  versus SCE was observed. This is attributable to a one electron reduction of one or both Rh(III) centers. The quasi-reversibility of the wave perhaps indicates a fast intermolecular dimerization of two Rh(II) centers [30]. Another reduction at  $-0.4\text{ V}$  versus SCE was observed. This reduction at a relatively high potential might be due to a rhodium mediated reduction of the tungstate ligand,  $\text{W}^{\text{VI}}/\text{W}^{\text{V}}$ , since the non-substituted zinc polyoxometalate starting material is reduced at only  $-0.7\text{ V}$  versus SCE, Fig. 4b. Alternatively, the two compounds may simply have different thermodynamic potentials. The redox behavior of the  $[(\text{WZnRh}_2^{\text{III}})(\text{ZnW}_9\text{O}_{34})_2]^{10-}$  polyanion is very much different from that reported for the rhodium substituted Keggin and Wells–Dawson compounds where no  $\text{Rh}^{\text{III}}/\text{Rh}^{\text{II}}$  reduction was reported and the potential curves were similar to the complete Keggin or Wells–Dawson polyanion [29].

#### 2.4. Catalytic activity

The oxidative catalytic activity of the  $[(\text{WZnRh}_2)(\text{ZnW}_9\text{O}_{34})_2]^{10-}$  polyanion was tested to compare its activity with other isostructural transition metal substituted polyoxometalates in reactions requiring activation of

hydrogen peroxide [26–28]. In order to carry out the desired catalytic tests in organic solvents, the alkali metal was exchanged with hydrophobic quaternary ammonium salts. Thus, the synthetic route to the methyltricaprylammonium salt of  $[(\text{WZnRh}_2)(\text{ZnW}_9\text{O}_{34})_2]^{10-}$  involves a methathetical exchange by addition of

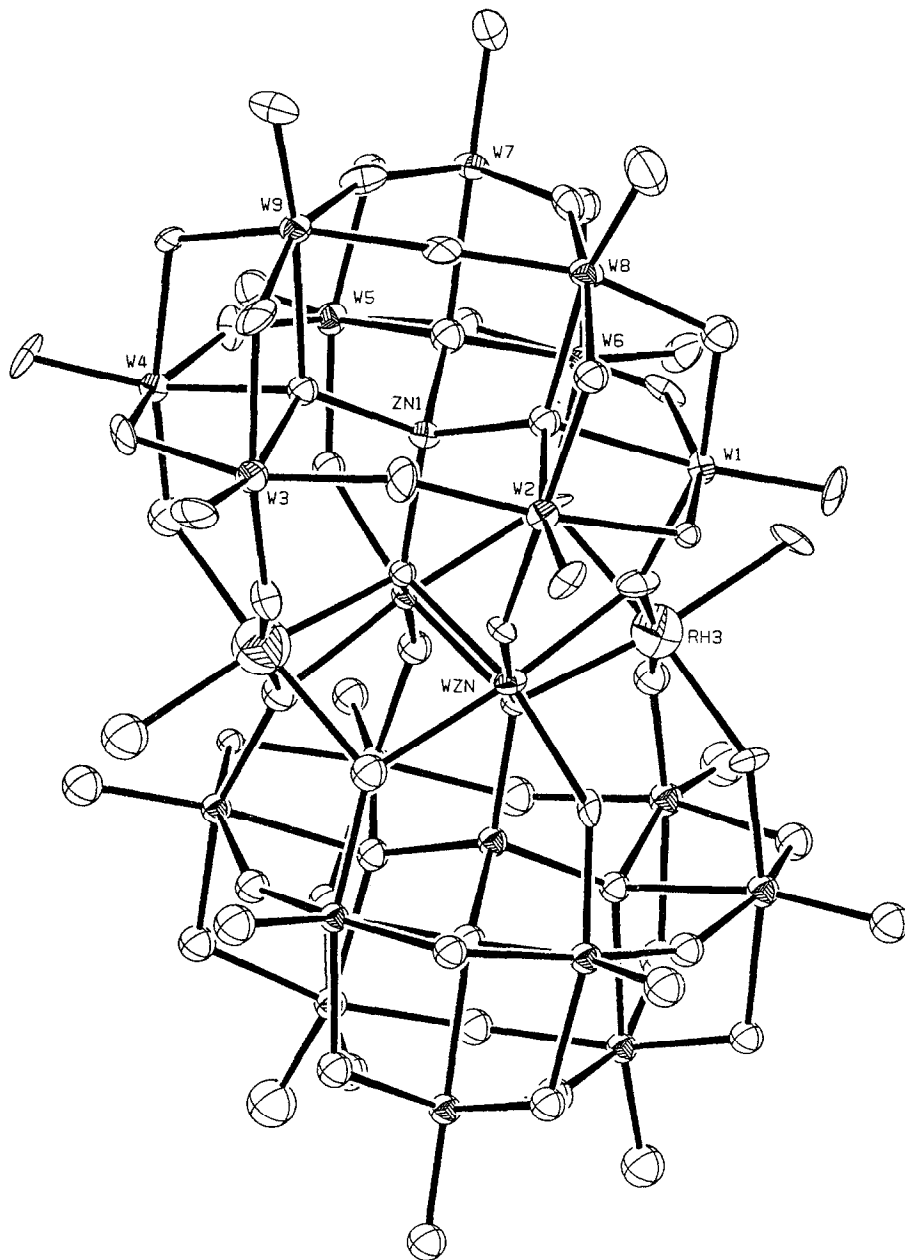


Fig. 1. Ortep view of  $[\text{ZnWRh}_2(\text{ZnW}_9\text{O}_{34})_2]^{10-}$ .

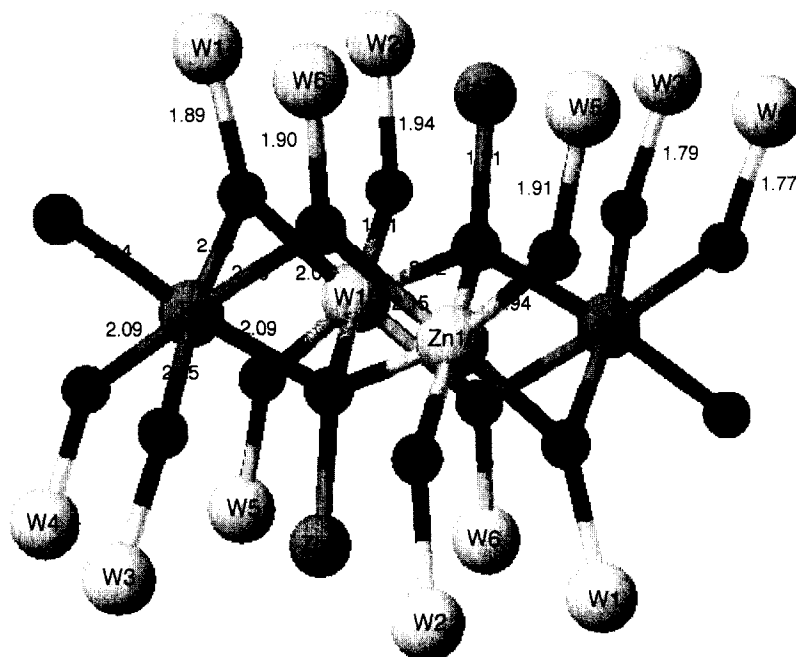


Fig. 2. Enlarged view of the central 'ring' of  $[\text{ZnWRh}_2^{\text{III}}(\text{ZnW}_9\text{O}_{34})_2]^{10-}$  with atomic bond distances.

a stoichiometric amount of methyltricaprylammonium chloride dissolved in 1,2-dichloroethane to an aqueous solution of the potassium salt of the polyoxometalate. A stoichiometric amount of ammonium salt was used to avoid having excess methyltricaprylammonium chloride in the final product. The now hydrophobic oily polyoxometalate, formally  $\text{Q}_{10}(\text{WZnRh}_2^{\text{III}})(\text{ZnW}_9\text{O}_{34})_2$  was isolated by evaporation of the solvent without further pu-

rification. The IR spectrum of the hydrophobic polyoxometalate in the region of  $1000\text{--}750\text{ cm}^{-1}$  is identical to that of the original sodium compound indicating that the polyoxometalate has retained its structure.

For the oxidation (epoxidation) of representative alkenes with 30%  $\text{H}_2\text{O}_2$ , a typical reaction

Table 1  
Crystallographic data for  $\text{Na}_{10}\text{Rh}_2^{\text{III}}(\text{H}_2\text{O})_2\text{Zn}_3\text{W}_{19}\text{O}_{68} \cdot 42\text{H}_2\text{O}$

|  |                        |
|--|------------------------|
| Space group                                      | $\text{P2}_1/\text{c}$ |
| $a$ (Å)  | 13.071 (3)             |
| $b$ (Å)  | 17.862 (5)             |
| $c$ (Å)  | 24.211 (5)             |
| $\beta$ (deg)                                    | 118.99 (2)             |
| $V$ (Å <sup>3</sup> )                            | 4944 (1)               |
| $Z$  | 2                      |
| $\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )      | 4.01                   |
| $\mu$ (Mo $\text{K}\alpha$ ) (cm <sup>-1</sup> ) | 236.98                 |
| Number of unique reflections                     | 9035                   |
| Number of reflections with $I \geq 3\sigma_I$    | 6544                   |
| $R$  | 0.050                  |
| $R_w$  | 0.069                  |

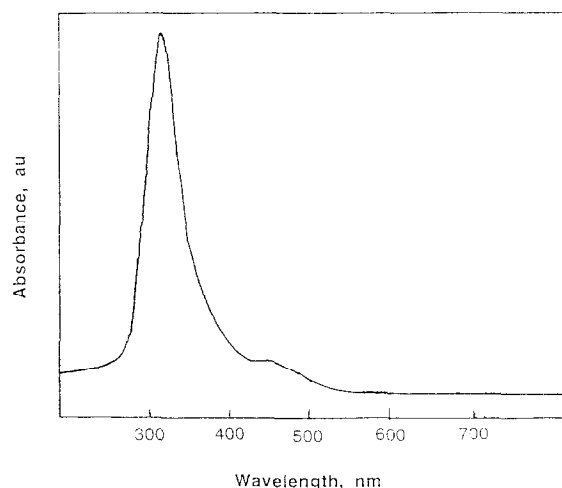


Fig. 3. UV-visible spectra of 0.12 mM  $\text{K}_{10}(\text{WZnRh}_2^{\text{III}})(\text{ZnW}_9\text{O}_{34})_2$  in water.

Table 2

Positional parameters and thermal coefficients for  $\text{Na}_{10}\text{Rh}_2^{\text{III}}(\text{H}_2\text{O})_2\text{Zn}_3\text{W}_9\text{O}_{68}\cdot 42\text{H}_2\text{O}$ 

| Atom         | x          | y          | z          | B(eq)   |
|--------------|------------|------------|------------|---------|
| W(1)         | 0.38251(9) | 0.22151(5) | 0.46464(5) | 1.21(4) |
| W(2)         | 0.61343(9) | 0.22414(6) | 0.44374(4) | 1.23(4) |
| W(3)         | 0.8940(1)  | 0.13428(6) | 0.56083(5) | 1.51(4) |
| W(4)         | 0.91028(9) | 0.05697(6) | 0.68562(5) | 1.43(4) |
| W(5)         | 0.6534(1)  | 0.05752(6) | 0.71427(5) | 1.35(4) |
| W(6)         | 0.40941(9) | 0.13233(5) | 0.60922(4) | 1.13(4) |
| W(7)         | 0.63366(9) | 0.23987(5) | 0.69861(4) | 1.34(4) |
| W(8)         | 0.6081(1)  | 0.32723(6) | 0.55354(5) | 1.42(4) |
| W(9)         | 0.89341(9) | 0.24283(6) | 0.67170(5) | 1.33(4) |
| Zn(1)        | 0.6397(2)  | 0.1281(1)  | 0.5750(1)  | 1.1(1)  |
| W(10) = WZn  | 0.4867(1)  | 0.03922(8) | 0.43819(6) | 1.14(5) |
| Zn(10) = WZn | 0.4867     | 0.0392     | 0.4382     | 1.1     |
| Rh           | 0.2677(3)  | 0.0331(2)  | 0.4621(1)  | 4.6(1)  |
| O(11)        | 0.237(2)   | 0.246(1)   | 0.4139(8)  | 2.2(7)  |
| O(12)        | 0.439(1)   | 0.2379(8)  | 0.4038(7)  | 0.9(3)  |
| O(13)        | 0.378(2)   | 0.1939(9)  | 0.5393(8)  | 1.5(6)  |
| O(14)        | 0.438(2)   | 0.322(1)   | 0.4966(8)  | 1.8(3)  |
| O(15)        | 0.573(1)   | 0.2128(9)  | 0.5189(7)  | 1.4(3)  |
| O(16)        | 0.379(2)   | 0.118(1)   | 0.4473(8)  | 1.8(7)  |
| O(21)        | 0.626(1)   | 0.248(1)   | 0.3787(7)  | 1.7(9)  |
| O(22)        | 0.768(9)   | 0.201(1)   | 0.5006(9)  | 2.1(7)  |
| O(23)        | 0.628(1)   | 0.326(1)   | 0.4780(7)  | 1.5(3)  |
| O(24)        | 0.576(1)   | 0.1182(9)  | 0.4292(7)  | 1.5(6)  |
| O(31)        | 0.996(2)   | 0.147(1)   | 0.5331(9)  | 2.7(8)  |
| O(32)        | 0.994(1)   | 0.082(1)   | 0.6388(8)  | 1.8(7)  |
| O(33)        | 0.956(1)   | 0.230(1)   | 0.6188(8)  | 2.3(7)  |
| O(34)        | 0.806(1)   | 0.1386(9)  | 0.6159(7)  | 1.3(3)  |
| O(35)        | 0.814(1)   | 0.053(1)   | 0.5185(8)  | 1.7(7)  |
| O(41)        | 1.025(1)   | 0.014(1)   | 0.7502(8)  | 2.1(7)  |
| O(42)        | 0.799(1)   | 0.0632(9)  | 0.7163(8)  | 1.6(6)  |
| O(43)        | 0.972(1)   | 0.1628(9)  | 0.7273(7)  | 1.5(6)  |
| O(44)        | 0.162(2)   | 0.019(1)   | 0.3650(8)  | 2.1(7)  |
| O(51)        | 0.683(2)   | 0.001(1)   | 0.7791(8)  | 2.2(7)  |
| O(52)        | 0.487(1)   | 0.0705(9)  | 0.6860(7)  | 1.5(3)  |
| O(53)        | 0.675(1)   | 0.55(1)    | 0.7580(8)  | 1.6(3)  |
| O(54)        | 0.592(1)   | 0.138(1)   | 0.6391(7)  | 1.5(3)  |
| O(55)        | 0.389(1)   | 0.0172(9)  | 0.3494(8)  | 1.4(6)  |
| O(61)        | 0.272(1)   | 0.132(1)   | 0.6032(8)  | 2.2(7)  |
| O(62)        | 0.469(1)   | 0.219(1)   | 0.6690(7)  | 1.7(3)  |
| O(63)        | 0.398(2)   | 0.48(1)    | 0.5590(7)  | 1.8(7)  |
| O(71)        | 0.654(2)   | 0.310(1)   | 0.7530(8)  | 2.0(7)  |
| O(72)        | 0.583(1)   | 0.300(1)   | 0.6288(8)  | 1.8(7)  |
| O(73)        | 0.780(2)   | 0.236(1)   | 0.7035(8)  | 1.9(7)  |
| O(81)        | 0.614(2)   | 0.425(1)   | 0.561(1)   | 3.2(9)  |
| O(82)        | 0.763(1)   | 0.298(1)   | 0.6049(8)  | 1.8(7)  |
| O(91)        | 0.976(2)   | 0.317(1)   | 0.7167(9)  | 2.5(8)  |
| O(10)        | 0.597(1)   | 0.0335(8)  | 0.5332(7)  | 1.0(3)  |
| O(Rh)        | 0.143(2)   | 0.105(1)   | 0.469(1)   | 2.9(8)  |
| Na(1)        | 0.326(1)   | 0.2477(7)  | 0.2867(5)  | 3.1(5)  |
| Na(2)        | 0.344(1)   | 0.4397(7)  | 0.3021(5)  | 3.9(5)  |
| Na(3)        | 0.244(1)   | 0.3804(7)  | 0.6803(6)  | 4.4(6)  |
| Na(4)        | 0.791(1)   | 0.0926(7)  | 0.3188(6)  | 3.4(5)  |
| Na(5)        | 0.046(1)   | 0.2292(7)  | 0.4054(5)  | 3.4(5)  |
| O(1W)        | 0.434(2)   | 0.165(1)   | 0.255(1)   | 5(1)    |
| O(2W)        | 0.215(2)   | 0.137(1)   | 0.277(1)   | 2.7(8)  |

Table 2 (continued)

| Atom   | x        | y        | z         | B(eq)  |
|--------|----------|----------|-----------|--------|
| O(3W)  | 0.760(2) | 0.449(1) | 0.7083(9) | 3.0(9) |
| O(4W)  | 0.459(2) | 0.345(1) | 0.287(1)  | 3.1(9) |
| O(5W)  | 0.214(2) | 0.339(1) | 0.305(1)  | 4(1)   |
| O(6W)  | 0.202(2) | 0.244(1) | 0.672(1)  | 3.5(9) |
| O(7W)  | 0.230(2) | 0.054(1) | 0.6943(9) | 2.8(8) |
| O(8W)  | 0.634(3) | 0.067(1) | 0.338(1)  | 5(1)   |
| O(9W)  | 0.980(2) | 0.136(1) | 0.3282(9) | 2.9(8) |
| O(10W) | 0.951(2) | 0.327(1) | 0.339(1)  | 4(1)   |
| O(11W) | 0.846(2) | 0.206(1) | 0.391(1)  | 4(1)   |
| O(12W) | 0.313(3) | 0.347(2) | 0.602(2)  | 8(2)   |
| O(13W) | 0.928(2) | 0.037(2) | 0.429(1)  | 6(1)   |
| O(14W) | 0.427(3) | 0.437(1) | 0.408(1)  | 4(1)   |
| O(15W) | 0.373(3) | 0.548(2) | 0.566(1)  | 6(1)   |
| O(16W) | 0.095(2) | 0.274(2) | 0.507(1)  | 6(1)   |
| O(17W) | 0.905(3) | 0.348(2) | 0.518(2)  | 9(2)   |
| O(18W) | 0.496(3) | 0.474(2) | 0.677(2)  | 7(2)   |
| O(19W) | 0.094(5) | 0.456(3) | 0.385(2)  | 6(1)   |
| O(20W) | 0.762(4) | 0.416(3) | 0.400(2)  | 13(1)  |
| O(21W) | 0.067(8) | 0.423(5) | 0.612(4)  | 11(1)  |

was carried out by stirring a biphasic mixture of 0.7 mmol of alkene and 0.2  $\mu\text{mol}$  of catalyst in 1.0 mL of 1,2-dichloroethane, and 2.0 mmol of

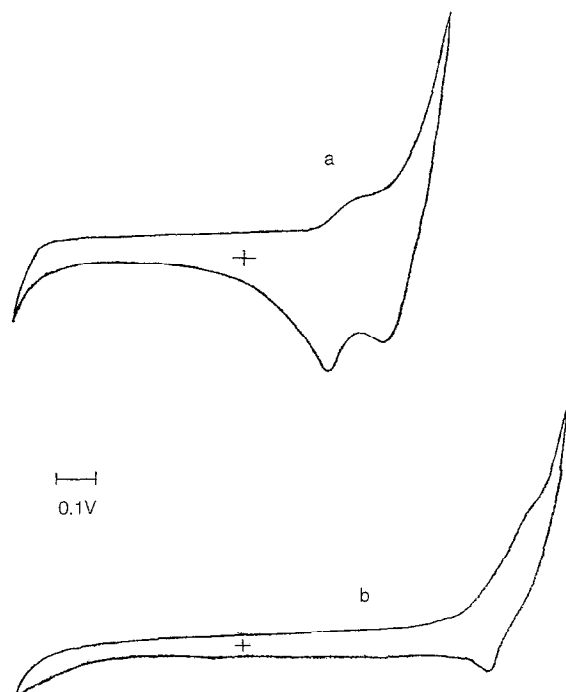


Fig. 4. Cyclic voltammograms of 3.3 mM  $\text{K}_{10}(\text{WZnRh}^{\text{II}})(\text{ZnW}_9\text{O}_{34})_2$  (a) and  $\text{Na}_{12}(\text{WZn}_3)(\text{ZnW}_9\text{O}_{34})_2$  (b) in 0.5 M NaCl at a glassy-carbon working electrode with reference calomel electrode at the voltage sweep rate 300 mV/s.

30% aqueous  $H_2O_2$ . After 24 h at  $25^\circ C$ , the products were identified and quantified by GC, GC/MS and iodometric analysis. Product distributions for the oxidation of representative alkenes oxidation with  $H_2O_2$  catalyzed by various active noble metal substituted polyoxometalates are summarized in Table 3. The results showed the following overall reactivities, i.e. conversion after 24 h: rhodium  $\sim$  palladium  $\sim$  platinum  $>$  ruthenium. Significantly, the rhodium compound, however, is much more selective in the epoxidation of cyclohexene with only slight formation of allylic oxidation products via a homolytic oxidation pathway. In this sense,  $[(WZnRh_2)(ZnW_9O_{34})_2]^{10-}$  most resembles the selectivity observed using the isostructural manganese polyoxometalate [26]. Indeed, the kinetic profile measured for the epoxidation of cyclooctene clearly shows, Fig. 5, that the

rhodium and manganese compounds have similar catalytic activity. Importantly, however, comparison of the rhodium and manganese polyoxometalates in terms of hydrogen peroxide yields also reveals from Fig. 5 that the new rhodium compound showed higher hydrogen peroxide yields to cyclooctene oxide.

As a final stage in this characterization of the catalytic activity of  $[(WZnRh_2)(ZnW_9O_{34})_2]^{10-}$ , the stability of the catalyst to aqueous 30% hydrogen peroxide was also evaluated by use of a combination of electronic UV-vis and addition of sequential portions of 30%  $H_2O_2$ . As shown in the case of the manganese catalyst [26] after 24 h of reaction at room temperature no decline in the concentration of the catalyst was observed as measured by the UV-vis spectrum, nor was there any change in the catalytic activity.

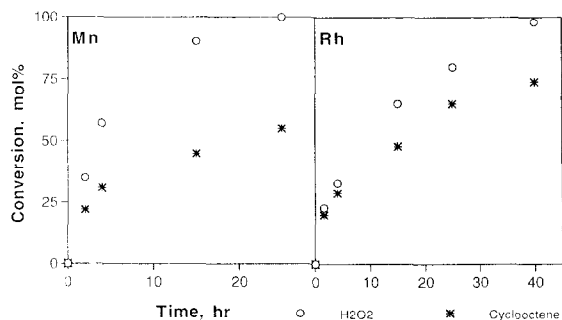


Fig. 5. Kinetic profile of cyclooctene epoxidation with 30%  $H_2O_2$  catalyzed by the rhodium and manganese substituted compounds. Reaction conditions: 0.8 mmol cyclooctene, 0.5  $\mu$ mol  $Q_{10}[ZnWRh_2(ZnW_9O_{34})_2]$  or  $Q_{12}[ZnWMn_2(ZnW_9O_{34})_2]$ , 0.8 mmol 30%  $H_2O_2$ , 1 mL  $C_2H_4Cl_2$ ,  $22^\circ C$ .

## 2.5. Mechanism

The similar reactivity of the rhodium and manganese analogs provides an additional tool in an attempt to understand the nature of the reactive catalytic intermediate in these peroxide mediated reactions. One school of thought on the reactivity of transition metal substituted polyoxometalates has coined them as 'inorganic porphyrins'. Especially noteworthy in this context are the oxidations with iodosobenzene [13,14], dioxygen binding [10] and isolation of chromium-oxo intermediates [11]. In these examples, oxidation or coordination chemistry at

Table 3  
Oxidation of alkenes by  $H_2O_2$  catalyzed by noble metals sandwich complexes<sup>a</sup>

| Alkene      | Products (conversion mol%) |                           |                              |                          |
|-------------|----------------------------|---------------------------|------------------------------|--------------------------|
|             | $[Pt_2Zn_3W_{19}O_{68}]$   | $[Pd_2Zn_3W_{19}O_{68}]$  | $[Rh_2Zn_3W_{19}O_{68}]$     | $[Ru_2Zn_3W_{19}O_{68}]$ |
| Cyclooctene | oxide (71)                 | oxide (76)                | oxide (75)                   | oxide (17)               |
| Cyclohexene | oxide (14)<br>enol (1)     | oxide (38)<br>enol (27)   | oxide (17)<br>enol (< 0.1)   | oxide (3)<br>enol (0.7)  |
| 1-Octene    | enone (16)<br>oxide (6.1)  | enone (30)<br>oxide (4.5) | enone (< 0.1)<br>oxide (5.0) | enone (4)<br>oxide (1.6) |

<sup>a</sup> Reaction conditions:  $25^\circ C$ , time 24 h,  $[Q_xM_2Zn_3W_{19}O_{68}] = 0.2 \mu$ mol, [alkene] = 0.7 mmol,  $[H_2O_2] = 2$  mmol in 1 mL  $C_2H_4Cl_2$ .

the tungsten framework atoms are easy to rule out. In the case of peroxide type oxidations, the situation is more complicated since both the tungsten framework atoms and the transition metal center may interact with hydrogen peroxide. In this manner, one may visualize a hydroperoxo or peroxy-tungstate intermediate on the one hand or a peroxy or oxo transition metal intermediate on the other hand. The fact that the rhodium and manganese compounds are similarly reactive in the system described above, whereas there is *no* rhodium porphyrin chemistry which parallels that of manganese porphyrin chemistry, argues well for an explanation basing the reactivity of these presently researched systems on a hydroperoxo or peroxy unit formed at a tungsten center.

The key questions which remain open, however, are which tungsten center is reactive and how does the transition metal substitution effect the reactivity. In this context it is important to recall that the non-substituted zinc compound is

not reactive [26]. Despite intense efforts, we have not been able to directly isolate any intermediates in these reactions for X-ray analysis. Therefore, we have sought other methods for resolution of these questions. Especially informative are the IR spectra of the manganese, rhodium and non-substituted (zinc) compounds before and after addition of hydrogen peroxide, Fig. 6. Thus, 1,2-dichloroethane solutions of polyoxometalate were treated with a thousand fold excess of 30% hydrogen peroxide for 30 min at room temperature; phases were separated and the organic phase was placed on a KBr plate followed by solvent evaporation. These spectra were compared with those of polyoxometalates without hydrogen peroxide treatment. The zinc polyoxometalate, Fig. 6a, was *unaffected* by addition of hydrogen peroxide with no evidence of formation of a peroxy intermediate. The rhodium substituted polyoxometalate, Fig. 6b, showed an important change upon addition of  $H_2O_2$ , notably the appearance

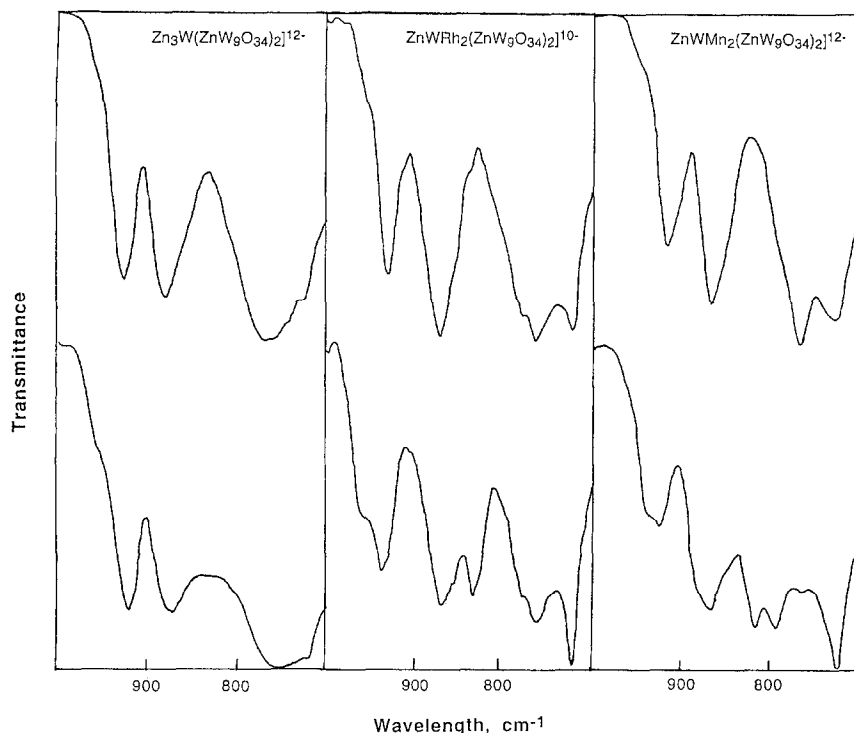


Fig. 6. IR spectra of  $Q_xM_2Zn_3W_{19}O_{68}$  before (top) and after treatment (bottom) with a thousand fold excess of  $H_2O_2$ .



of a new peak at  $835\text{ cm}^{-1}$ . A similar change could be observed in the manganese substituted compound, Fig. 6c, where a new maximum was observed at  $818\text{ cm}^{-1}$  along with the disappearance of the peak at  $768\text{ cm}^{-1}$ . Both the  $835$  and  $818\text{ cm}^{-1}$  absorptions can be attributed to peroxy species. In both the rhodium and manganese case addition of cyclooctene to the peroxy complex turns the IR spectrum back to the original one.

The fact that the zinc compound was inactive and showed no formation in the IR of a peroxy intermediate shows that the periphery or cap tungsten atoms (Fig. 1, W7, W8 and W9) in the  $\text{B}[\text{ZnW}_9\text{O}_{34}]^{12-}$  fragments do not appear to be relevant for catalytic activity. The fact that both the rhodium and manganese compounds were active and showed changes in the IR spectra upon addition of hydrogen peroxide, places the active site in the vicinity of the transition metal center. From the structure and bond distances as shown in Fig. 2, the most relevant tungsten atoms are W1, W6, W3, W4 and WZn. It is also significant that although both the rhodium and manganese compounds showed changes upon

the addition of hydrogen peroxide, the peroxy intermediates formed are different ( $835$  versus  $818\text{ cm}^{-1}$ ). This seems to indicate a role for the transition metal center in the activation of the suggested hydroperoxy or peroxy–tungstate active intermediate.

A further observation made in the course of the research indicates that the catalytic center is sterically hindered. Thus, 2,3-dimethyl-2-butene was significantly more reactive than 2-methyl-2-pentene (1230 versus 720 turnovers after 24 h using conditions described in Fig. 5) as would be expected for a nucleophilic–electrophilic interaction between the alkene and peroxy intermediate. However, cyclohexene was significantly more reactive than 1-methylcyclohexene (580 versus 205 turnovers after 24 h) and  $\alpha$ -pinene was unreactive. This observation indicates strong steric constraint at the catalytic center. Assuming the polyoxometalate retains its structural integrity throughout the catalytic cycle as borne out by the high stability, a further speculative interpretation as delineated in Fig. 7, can be illustrated. Thus, a sterically hindered active site is formed upon formation

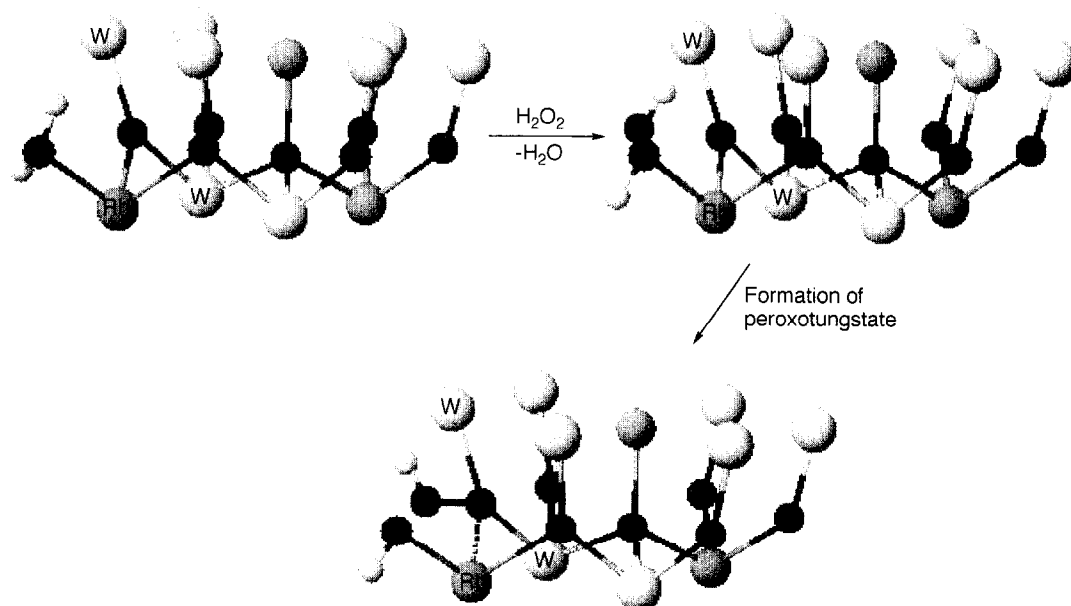


Fig. 7. Speculative illustration of the formation of the active peroxy species.

upon the coordination of a peroxo ligand at the O63 or O16 positions in the original polyoxometalate. This position was chosen due to the proximity to the rhodium (manganese) center where initial ligation may occur and the fact these are the only oxygen positions in close contact with three metal atoms as opposed to two metal atoms in all other cases. Interaction of a peroxo oxygen with three metal centers may increase its electrophilicity leading to increased reactivity. Initial ligation or interaction of hydrogen peroxide with the substituted transition metal center certainly plays a role in the entire series of these isostructural compounds as this interaction may lead, in the relevant cases, to homolytic cleavage of hydrogen peroxide which in turn determines both yield and selectivity.

### 3. Experimental section

#### 3.1. Preparation of polyoxometalates

The zinc precursor compound,  $\text{Na}_{12}\text{Zn}_3(\text{H}_2\text{O})_2\text{Zn}_2\text{W}_{19}\text{O}_{68} \cdot 46\text{H}_2\text{O}$  and the manganese, ruthenium, platinum and palladium substituted compounds were synthesized according to the procedures described in the literature [23,27] with satisfactory elementary analyses. The new rhodium(III) substituted compound was prepared by the following procedure. A solution of 2.2 g (0.35 mmol) of  $\text{Na}_{12}\text{Zn}_3(\text{H}_2\text{O})_2\text{Zn}_2\text{W}_{19}\text{O}_{68} \cdot 46\text{H}_2\text{O}$  in 20 mL of water was prepared and heated to 90°C; 0.25 g (0.88 mmol, 2.5 eq.)  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  was added. The solution was stirred at this temperature for 4 h and then cooled. The insoluble residue was filtered off and the mother liquor (filtrate) was treated by the addition of 2 g of KCl. After the dissolution of the KCl, the potassium salt of the polyoxometalate was precipitated almost immediately in a yield of 0.85 g. The product was recrystallized twice from hot water, giving an overall yield of 27%. Potassium was analyzed by atomic absorption (single beam GBC 903)

and water was determined by thermogravimetry (Mettler 50) prior to polyoxometalate decomposition using boiling 1 M NaOH overnight. Zinc and rhodium were analyzed by atomic absorption whereas tungsten was determined gravimetrically via the quinolate. Analysis for  $\text{K}_{10}(\text{WZnRh}^{\text{III}})(\text{ZnW}_9\text{O}_{34})_2 \cdot 40\text{H}_2\text{O}$ : Calcd (found) K, 6.38 (6.05); Rh, 3.37 (3.40); Zn, 3.19 (3.24); W, 57.15 (57.67). The sodium salt used for X-ray diffraction studies was obtained by dissolution of potassium salt into a saturated solution of sodium nitrate at room temperature. Slow evaporation over a period of one week yield single crystals adequate for X-ray structure determination. The quaternary ammonium salts of the polyoxometalates were prepared by methathetical exchange with tricaprylmethyl ammonium chloride (Aliquot 336). For example,  $\text{Q}_{10}[(\text{WZnRh}^{\text{III}})(\text{ZnW}_9\text{O}_{34})_2]$  was prepared by mixing 0.1 mmol  $\text{K}_{10}(\text{WZnRh}^{\text{III}})(\text{ZnW}_9\text{O}_{34})_2 \cdot 40\text{H}_2\text{O}$  dissolved in 3 mL water and 10 equivalents of Aliquot 336 dissolved in 5 mL 1,2-dichloroethane followed by phase separation, drying of the organic phase with  $\text{Na}_2\text{SO}_4$  and preparation of a stock solution.

#### 3.2. X-ray determination

Data were measured on a PW1100/20 Philips Diffractometer.  $\text{Mo K}_\alpha$  ( $\lambda = 0.71069 \text{ \AA}$ ) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range of  $11 \leq \theta \leq 15^\circ$ . Intensity data were collected using the  $\omega - 2\theta$  technique to a maximum of  $2\theta$  of  $50^\circ$ . The scan width,  $\Delta\omega$ , for each reflection was  $1.00 + 0.35 \tan \theta$  with a scan speed of 3.0 deg/min. Background measurements were made for a total of 10 s at both limits of each scan. Three standard reflections were monitored every 60 min with no systematic variations being found. Intensities were corrected for Lorentz, polarization and absorption effects. All non-hydrogen atoms were found using the SHELXS-86

method. After several cycles of refinements the positions of the hydrogen atoms were calculated and added to the refinement process. Refinement proceeded to convergence by minimizing the function  $\sum w(|F_o| - |F_c|)^2$ . A final difference Fourier synthesis map showed several peaks less than  $2.5 \text{ e}/\text{\AA}^3$  scattered about the unit cell without significant feature. The discrepancy indices were calculated by  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ . The pertinent crystallographic data are presented in Table 1.

### 3.3. Physical properties

The electronic absorption spectra were recorded on a Hewlett-Packard Model 8452A diode-array UV–visible spectrometer in water or 1,2-dichloroethane as solvents. Infrared spectra were recorded on a Nicolet 510M instrument. The spectra of the original alkali salts were taken as 2 wt% mixtures in KBr pellets. Those of the quaternary ammonium salts were taken directly after evaporation of the solvent on a KBr plate both before and after treatment of the organic phase with aqueous hydrogen peroxide. Cyclovoltammetric measurements were carried out with BAS CV-1B instrument using a glassy carbon working electrode, a calomel reference electrode, and 0.5 M NaCl supporting electrolyte in water solution.

### 3.4. Characterization catalytic oxidation activity with hydrogen peroxide

The solvent, substrates and hydrogen peroxide were analytical grade from common commercial sources. Reaction progress for the rate law studies between cyclooctene and hydrogen peroxide was monitored using gas chromatography. The most effective GC conditions (Hewlett-Packard 5890) for the rapid quantification of products for the reactions of the alkenes involved the use of a 5% phenyl methyl silicone fused-silica capillary column, helium as the carrier gas, and temperature programming. Reac-

tions were carried out in 5 mL vial equipped with cap and a stirring bar. Catalyst and substrate were dissolved in 1,2-dichloroethane, hydrogen peroxide was added and the progress reaction was monitored by GC. Typically, substrate (0.7 mmol) was added to the solution of catalyst (0.2  $\mu\text{mol}$ ) in 1 mL of  $\text{C}_2\text{H}_4\text{Cl}_2$  followed by 0.2 mL of 30% aqueous  $\text{H}_2\text{O}_2$ . The resulting biphasic mixture was stirred at  $25^\circ\text{C}$ . GLC analysis for the organic compounds was performed on aliquots withdrawn directly from the reaction mixture. Hydrogen peroxide was determined by iodometric titration whereby an aliquot of the reaction mixture was dissolved in 95% ethanolic NaI containing 10% of acetic acid. From the absorbance of  $\text{I}_3^-$  at 360 nm ( $\epsilon = 3.4 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) 100% of the theoretical 2 equiv/mol  $\text{H}_2\text{O}_2$  was titrated.

### Acknowledgements

This research was supported by the Basic Research Foundation administered by the Israel Academy of Sciences and Humanities. Dr. Shmuel Cohen is thanked for the X-ray diffraction studies.

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