ELSEVIER

Journal of Molecular Catalysis A: Chemical 137 (1999) 127–133

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

$Mn^{III}L_x$/*t*-BuOOH-induced activation of dioxygen for the oxygenation of cyclohexene

Takayuki Matsushita [a], Donald T. Sawyer [b], Andrzej Sobkowiak [c,*]

[a] *Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-21, Japan*
[b] *Department of Chemistry, Texas A&M University, College Station, TX 77843, USA*
[c] *Faculty of Chemistry, Rzeszow University of Technology, 35-959 Rzeszow, Poland*

Received 20 October 1997; accepted 5 March 1998

Abstract

Several manganese (III) complexes ($Mn^{III}L_x$) in combination with *tert*-butyl hydroperoxide (*t*-BuOOH) activate dioxygen (O_2) to oxygenate cyclohexene (*c*-C_6H_{10}) to its ketone, alcohol, and epoxide. The product profiles depend on the ligand and solvent matrix. With picolinate (PA), bipyridine (bpy), or triphenylphosphine oxide ($OPPh_3$) as the ligand in py/HOAc (2:1 molar ratio) dominant product is the ketone [*c*-C_6H_8(O)] whereas Schiff–base complexes produce *c*-C_6H_8(O), *c*-C_6H_9(OH) and the epoxide in almost equal yields. However, in MeCN *c*-C_6H_8(O) is the dominant product for all of the complexes.

Keywords: Manganese complexes; Dioxygen; Cyclohexene; Oxygenated Fenton chemistry; Dioxygen activation

1. Introduction

The chemistry of manganese complexes is of fundamental interest because of their important role as catalysts in industrial processes and biological systems. Several reviews have summarized these aspects of manganese chemistry; the biochemistry of manganese [1–6] the catalytic oxidation/oxygenation of organic substrates [7–11] (including epoxidation) [12–14], selective DNA cleavage [15–17], models of the photosystem-II oxidation of water [18–22], interaction with dioxygen [23], and binuclear manganese complexes as bleaching agents [24].

Previous work [25] has demonstrated that in a pyridine/acetonitrile solvent matrix the [$Cu^I(bpy)_2^+$] complex activates hydrogen peroxide [HOOH] and *tert*-butyl hydroperoxide [*t*-BuOOH] for the selective ketonization of the methylenic carbons in hydrocarbon substrates. With 5 mM $Cu^I(bpy)_2^+$ and 10 mM *t*-BuOOH under argon the conversion efficiency [100% represents one ketone per two HOOH(Bu-*t*) molecules and/or one alcohol per one HOOH or *t*-BuOOH] for cyclohexane (*c*-C_6H_{12}) is 10% and for ethylbenzene ($PhCH_2CH_3$) is 140%. However, in the presence of O_2 the conversion efficiency for *c*-C_6H_{12} increases to 67% and for $PhCH_2CH_3$ to 440%, respectively. This represents a $Cu^I(bpy)_2^+$/*t*-BuOOH-induced autoxygenation with at least 2.2-O_2/catalyst turnovers.

* Corresponding author.

1381-1169/99/$ - see front matter
PII: S1381-1169(98)00109-5

A series of subsequent papers [26–29] confirmed that when excess HOOH (or *t*-BuOOH) is combined with several transition metal complexes, it becomes the dominant substrate for the initially formed Fenton intermediate (**1**) [30,31]

$$L_xM + \mathrm{HOOH} \xrightarrow{\mathrm{py}} \left[L_x^- M\mathrm{OOH}(\mathrm{pyH}^+) \right] (\mathbf{1}) \quad (1)$$

to produce dioxygen

$$\mathbf{1} + \mathrm{HOOH} \rightarrow L_xM + \mathrm{O_2} + \mathrm{H_2O} \quad (2)$$

with the subsequent formation of the reactive intermediate for oxygenated Fenton chemistry.

$$\mathbf{1} + \mathrm{O_2} \rightleftarrows \mathbf{1}(\mathrm{O_2}) \quad (3)$$

To our surprise, coordinately unsaturated iron(II) complexes [e.g., $Fe^{II}(bpy)_2^{2+}$ and $Fe^{II}(OPPh_3)_4^{2+}$] in acetonitrile catalytically activate dioxygen for the direct oxygenation of cyclohexene and methyl linoleate [$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7C(O)OCH_3$] [32]. With 4 M *c*-$C_6H_{10}$ as a substrate the combination of 1 mM $Fe^{II}(bpy)_2^{2+}$ and 1 mM O_2 undergoes 230 turnovers within 1 h to yield 2-cyclohexen-1-one [*c*-$C_6H_8(O)$], 2-cyclohexen-1-ol [*c*-C_6H_9OH], and the epoxide [cyclohexane oxide, *c*-$C_6H_{10}O$] in an approximate 20:20:1 ratio. However, the $Fe^{II}(bpy)_2^{2+}/t$-$BuOOH/O_2$ system (oxygenated Fenton chemistry) does not yield any epoxide with *c*-C_6H_{10} as a substrate. The effectiveness of the iron systems has prompted a systematic investigation to characterize the L_xMn/t-$BuOOH/O_2$ system and its reactivity toward organic substrates.

2. Experimental section

2.1. Equipment

The reaction products were separated and identified with a Hewlett-Packard 5880A Series gas chromatograph with a FID detector or by a Hewlett-Packard 5790A series gas chromatograph with a mass-selective detector. Both were equipped with a HP-1 capillary column (cross-linked methyl silicone gum phase 12 m × 0.2 mm i.d.).

2.2. Chemicals and reagents

The reagents for the investigations and syntheses were commercially available of the highest purity and used without further purification. Burdick and Jackson 'distilled in glass' grade acetonitrile (MeCN, 0.004% H_2O), pyridine (py, 0.014% H_2O) and glacial acetic acid (HOAc, ACS grade, Fisher) were used as solvents. All solid compounds were dried in vacuo over $CaSO_4$ for 24 h prior to use. The $[Mn^{II}(MeCN)_4](ClO_4)_2$ complex was prepared by multiple recrystallization of $[Mn^{II}(H_2O)_6](ClO_4)_2$ from MeCN. The tetradentate Schiff bases: *N*,*N*′-disalicylidene-1,2-diaminoethane (H_2salen), *N*,*N*′-disalicylidene-1,3-diaminopropane (H_2salpn), and *N*,*N*′-disalicylidene 1,2-diaminobenzene (H_2salphen) were synthesized by standard methods (Schiff base condensation of 2 moles of the salicylaldehyde with 1 mole of appropriate diamine). Mn^{III}(salen)Cl, Mn^{III}(salpn)Cl(H_2O), and Mn^{III}(salphen)Cl complexes were obtained by reacting the respective ligand with $Mn(OAc)_3 \cdot H_2O$ and LiCl in alcoholic solution [33,34]. Other complexes were prepared in situ by mixing $[Mn^{II}(MeCN)_4](ClO_4)_2$, $Mn(OAc)_2$, or $Mn(OAc)_3 \cdot 2H_2O$ with stoichiometric ratios of the ligands; picolinic acid (PAH), 2,6-pyridinedicarboxylic acid ($DPAH_2$), 2,2′-bipyridine (bpy), triphenylphosphine oxide ($OPPh_3$), and a tetradentate Schiff base.

2.3. Methods

The substrate (1 M) and the appropriate complex (either pre-synthesized or prepared in situ) were combined with the solvent (total volume = 5 ml) followed by the addition of dioxygen

Table 1
Mn(II), Mn(III)/*t*-BuOOH-induced activation of O_2 for the oxygenation of cyclohexene (*c*-C_6H_{10}) in MeCN[a]

Complex, 5 mM	O_2 (atm)	Products (mM ± 5%)			
		c-C_6H_8(O)	*c*-C_6H_9OH	*c*-$C_6H_{10}O$ (epoxide)	Efficiency[c] (%)
$Mn^{III}(PA)_2(OAc)$	0	3	6	0.8	49
$Mn^{III}(PA)_2(OAc)$	1.0	103	37	7	735
$Mn^{III}(OPPh_3)_4(OAc)_3$	0	4	3	0	35
$Mn^{III}(OPPh_3)_4(OAc)_3$	1.0	48	28	0	380
$Mn^{II}(bpy)_2(OAc)_2$	0	2	0	1	15
$Mn^{II}(bpy)_2(OAc)_2$	1.0	62	22	8	460
$Mn^{III}(bpy)_2(OAc)_3$	0	12	6	0	90
$Mn^{III}(bpy)_2(OAc)_3$	0.2	26	14	0.5	202
$Mn^{III}(bpy)_2(OAc)_3$	1.0	139	41	5	925
Mn^{III}(salen)(OAc)	0	5	1	0	30
Mn^{III}(salen)(OAc)	0.2	29	12	1	210
Mn^{III}(salen)(OAc)	1.0	159(275)[b]	48(57)[b]	6(15)[b]	1065(1735)[b]
Mn^{III}(salphen)(OAc)	0	8	4	0	60
Mn^{III}(salphen)(OAc)	1.0	41(154)[b]	16(45)[b]	1(8)[b]	290(1035)[b]
Mn^{III}(salen)Cl, 1 mM	1.0	12	5	0	85
Mn^{III}(salphen)Cl, 1 mM	1.0	32(67)[b]	9(17)[a]	0.4(0.7)[b]	207(423)[b]
Mn^{III}(salpn)Cl, 1 mM	1.0	5(60)[b]	3(39)[b]	0(1)[b]	40(500)[b]

[a]Concentrations of *t*-BuOOH and the substrate (*c*-C_6H_{10}) were in all cases equal to 20 mM and 1 M, respectively. Yields of the products were measured after 3 h.
[b]Yields of the products after 24 h.
[c]Efficiency for product formation, mM of products per mM of *t*-BuOOH (100% represents one product species per *t*-BuOOH).

Table 2
Mn(II), Mn(III)/*t*-BuOOH-induced activation of O_2 for the oxygenation of cyclohexene in 2:1 py/HOAc[a]

Complex, 10 mM	O_2 (atm)	Products (mM ± 5%)			
		c-C_6H_8(O)	*c*-C_6H_9OH	*c*-$C_6H_{10}O$ (epoxide)	Efficiency[b] (%)
$Mn^{II}(PA)_2$	0	4	2	1	35
$Mn^{II}(PA)_2$	1.0	27	8	3	190
$Mn^{III}(PA)_2(OAc)$	0	10	2	0.5	62
$Mn^{III}(PA)_2(OAc)$	1.0	32	4	1	185
$Mn^{II}(DPAH)_2$	0	0	0	0	0
$Mn^{II}(DPAH)_2$	1.0	2	0.5	0	12
$Mn^{III}(DPAH)_2(OAc)$	0	1	< 0.5	0	7
$Mn^{III}(PA)_2(OAc)$	1.0	21	5	0	135
$Mn^{II}(OPPh_3)_4(OAc)_2$	0	0	0	0	0
$Mn^{II}(OPPh_3)_4(OAc)_2$	1.0	7	2	0.6	48
$Mn^{III}(OPPh_3)_4(OAc)_3$	0	9	3	0	60
$Mn^{III}(OPPh_3)_4(OAc)_3$	1.0	111	12	3	630
$Mn^{II}(bpy)_2(OAc)_2$	0	< 0.5	0	0	2
$Mn^{II}(bpy)_2(OAc)_2$	1.0	14	2	0	80
$Mn^{III}(bpy)_2(OAc)_3$	0	9	3	0	60
$Mn^{III}(bpy)_2(OAc)_3$	1.0	96	10	2	108
Mn^{III}(salen)(OAc), 5 mM	1.0	22	19	18	295
Mn^{III}(salen)(OAc), 20 mM	1.0	24	25	30	395
Mn^{III}(salen)Cl	1.0	21	26	24	355
Mn^{III}(salphen)Cl	1.0	15	23	18	280
Mn^{III}(salpn)Cl	1.0	2	3	1	30

[a]Concentrations of *t*-BuOOH and the substrate (*c*-C_6H_{10}) were in all cases equal to 20 mM and 1 M, respectively. Yields of the products were measured after 3 h.
[b]Efficiency for product formation; mM of products per mM of *t*-BuOOH (100% represents one product species per *t*-BuOOH).

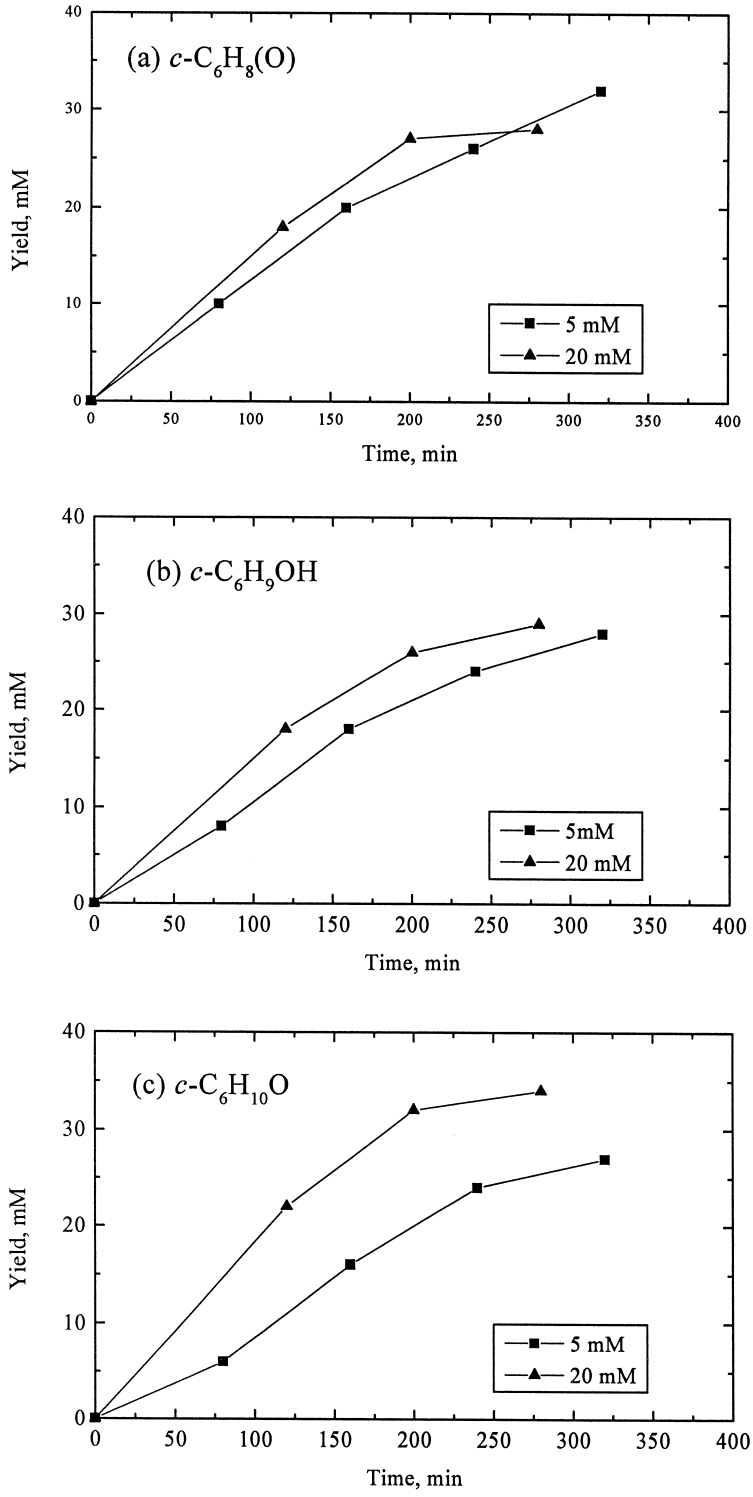


Fig. 1. Product yields from c-C_6H_{10}: (a) 2-cyclohexen-1-one [c-$C_6H_8(O)$], (b) 2-cyclohexen-1-ol [c-C_6H_9OH]; and (c) cyclohexane oxide [c-$C_6H_{10}O$] in the Mn^{III}(salen)(OAc)(5 mM or 20 mM)/t-BuOOH (20 mM)/O_2 (1 atm) system in 2:1 py/HOAc.

(O_2, 1 atm), air (0.2 atm, O_2), or high-purity argon gas (0 atm, O_2). The reaction cell (25-ml vial with cut-out cap and Teflon-faced septum) had a 20-ml head space, which provided a reservoir to maintain a constant solution concentration of dioxygen. For hydroperoxide activation, *t*-BuOOH (5-6 M solution in decane, its analytical concentration was determined iodometrically [35]), was injected to give a 20-mM concentration. The reactions were allowed to proceed for 3 or 24 h with constant stirring at room temperature (24 ± 2°C), after which samples from the reaction solutions (0.2 μl) were injected into a capillary-column gas chromatograph, with FID detector, for analysis. The progress of the reaction was monitored by withdrawal of an aliquot (0.2 μl) of the reaction mixture for injection into the GC. The characterization of the products by GC–MS was done after the reaction was quenched with water and the products were extracted with diethyl ether. Authentic samples were always used to confirm product identifications and to produce standard curves for quantitative assays of the product species. Biphenyl (10 mM) was used as an internal standard.

3. Results

The reaction efficiencies and product profiles for the activation of dioxygen, to oxygenate cyclohexene (*c*-C_6H_{10}) via various manganese/*t*-BuOOH combinations in MeCN and 2:1 py/HOAc are summarized in Tables 1 and 2. In the absence of dioxygen (under an argon atmosphere), where *t*-BuOOH is the sole oxidant, the reaction efficiencies usually are below 10%, and only occasionally, approach 60%. However, in the presence of dioxygen or air the efficiencies for product formation are greater than 200%. This clearly indicates that dioxygen is involved in the oxygenation process. Moreover, the time-dependent product profiles for the $Mn^{III}(bpy)_2(OAc)_3$ and Mn^{III}(salen)(OAc) complexes in MeCN indicate that the reactions are first-order with respect to the concentration of dioxygen. The latter complex in the most remarkable example of the activation of dioxygen for oxygenation of cyclohexene. In the system, more than 10 product molecules are produced per *t*-BuOOH. When the solvent is changed to 2:1 py/HOAc the overall efficiency is reduced by the factor of 3. However, whereas the ketone is the dominant product in acetonitrile, equal amounts of ketone, alcohol, and epoxide are produced in py/HOAc (about 4 product molecules/*t*-BuOOH). The results presented in Tables 1 and 2 indicate that Mn(II) complexes are less effective catalysts in comparison to their Mn(III) analogues. When HOOH is used in place of *t*-BuOOH, all of the systems fail to produce detectable amounts of product. Fig. 1 illustrates the product yields versus time for the oxygenation of cyclohexene that is catalyzed by the Mn^{III}(salen)/*t*-BuOOH/O_2 sys-

Table 3
$Mn(^{III})L_x$/*t*-BuOOH-induced activation of O_2 for the oxygenation of ethylbenzene ($PhCH_2CH_3$)[a]

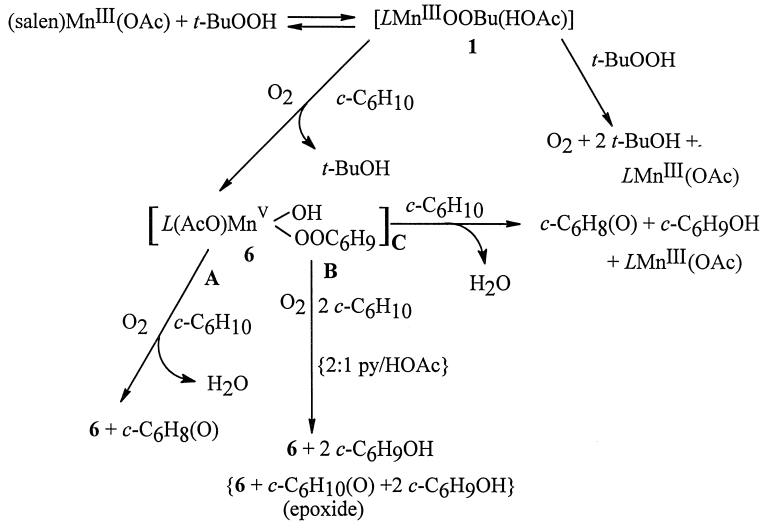
$Mn(^{III})L_x$	Solvent	Products (mM ± 5%)		
		$PhC(O)CH_3$	$PhCH(OH)CH_3$	Efficiency[b] (%)
5 mM $Mn^{III}(bpy)_2(OAc)_3$	MeCN	32	0	160
5 mM Mn^{III}(salen)(OAc)	MeCN	40	0	200
5 mM Mn^{III}(salen)(OAc)	2:1 py/HOAc	14	7	105
20 mM Mn^{III}(salen)(OAc)	2:1 py/HOAc	23	9	160
5 mM $Mn^{III}(OPPh_3)_4(OAc)_3$	2:1 py/HOAc	25	0	125

[a]Concentrations of *t*-BuOOH and the substrate (*c*-C_6H_{10}) were in all cases equal to 20 M and 1 M, respectively. Yields of the products were measured after 3 h.
[b]Efficiency for product formation; mM of products per mM of *t*-BuOOH (100% represents one product species per *t*-BuOOH).

tem in 2:1 py/HOAc solvent. In a 3-h period there is a constant increase in product yields, which are almost independent of the complex concentration. The deviation from linearity is probably due to the depletion of dioxygen. The investigated complexes do not react with cyclohexane (c-C_6H_{12}) but exhibit catalytic activity towards $PhCH_2CH_3$ (Table 3). The dominant product from the oxygenation of $PhCH_2CH_3$ in the $Mn^{III}L_x/t$-BuOOH/O_2 system is acetophenone [$PhC(O)CH_3$], but small amounts of *sec*-phenethyl alcohol [$PhCH(OH)CH_3$] often are formed.

4. Discussion

The results indicate that in the absence of dioxygen (under an argon atmosphere) neither Mn(II) nor Mn(III) complexes show substantial catalytic activity. The reaction efficiencies are small, and in some cases (mainly with L_xMn^{II}) no product is detected. However, under a dioxygen atmosphere, cyclohexene is effectively converted to the corresponding ketone, alcohol, and epoxide by L_xMn^{III}/t-BuOOH systems. The product profiles depend on the ligands and solution matrix. The Mn(III) complexes with PA, bpy, and $OPPh_3$ in py/HOAc (2:1 molar ratio) yield c-$C_6H_8(O)$ as the dominant product, whereas those with Schiff bases yield c-$C_6H_8(O)$, c-C_6H_9OH, and epoxide in almost equal yields. However, c-$C_6H_8(O)$ in MeCN is the dominant product for all of the manganese complexes. Excess *t*-BuOOH, when combined with a Mn(III) complex, initially produces its own O_2 atmosphere. Usually, about 50% of the added peroxide is decomposed (slowly the case of *t*-BuOOH) to O_2 via reactive intermediate **1** (Scheme 1). The liberated dioxygen becomes the oxygenate in the system and reacts with species **1** and the substrate to yield the observed products. Therefore, the yields of products under an argon atmosphere are usually less than 50%. With an excess of O_2 (under an O_2 atmosphere) most of the species **1** react with substrate to form species **6**. For substrates with weak C–H bonds in their methylenic groups ($PhCH_2CH_3$ and the allylic carbons of cyclohexene) intermediate **6** becomes a catalyst for the activation dioxygen. Clearly, when the reaction efficiency for such substrates is greater than 100% (products per *t*-BuOOH) the intermediate must activate O_2 for reaction with the substrate. Scheme 1 presents a reasonable proposed mechanism for the reactions in the system. Note that



Scheme 1. $Mn^{III}L_x/t$-BuOOH-induced activation of O_2 for the oxygenation of olefins.

the reactive intermediates are within square brackets because their formulations are hypothetical, although chemically reasonable, and are supported by electrochemical measurements [26] and consistent with the product profiles. In contrast to iron systems [26], the manganese(III) complexes apparently do not form species **6** in the presence of cyclohexane. This probably is due to the relatively large of C–H bond energies in *c*-C_6H_{12} ($\sim$ 96 kcal mol^{-1}) in comparison to the energy of the allylic C–H bonds in *c*-C_6H_{10} ($\sim$ 85 kcal mol^{-1}) and of the methylenic C–H bonds in $PhCH_2CH_3$ ($\sim$ 85 kcal mol^{-1}).

The present results confirm that transition-metal complexes undergo nucleophilic addition by hydroperoxides to form $[L_xMOOH(BH^+)]$ (**1**), which in the presence of dioxygen oxygenates hydrocarbons. However, the product profiles depend on the transition metal and its valence state, ligand, and solution matrix.

Acknowledgements

This work was supported by the Welch Foundation under Grant No. 1042A (D.T.S.) as well as by NATO Linkage Grant HTECH.LG 951559 (A.S. and D.T.S.).

References

[1] L. Que, A.E. True, Prog. Inorg. Chem. 38 (1990) 72.
[2] G. Renger, T. Wydrzynski, Biol. Met. 4 (1991) 73.
[3] A.W. Rutherford, A. Bonssac, J.L. Zimnermann, New J. Chem. 15 (1991) 491.
[4] A.Y. Sychiov, V.G. Isac, Russ. Chem. Rev. 62 (1993) 279.
[5] G.C. Dismukes, Chem. Rev. 96 (1996) 2909.
[6] V.K. Yachandra, K. Sauer, M.P. Klein, Chem. Rev. 96 (1996) 2927.
[7] G.G. Melikyan, Synthesis 833 (1993) .
[8] T. Mukaiyama, T. Yamada, Bull. Chem. Soc. Jpn. 68 (1995) 17.
[9] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
[10] R. Hage, Rec. Trav. Chim. Pays-Bas 115 (1996) 385.
[11] J. Mlochowski, S.B. Said, Pol. J. Chem. 71 (1997) 149.
[12] D. Ostovic, T.C. Bruice, Acc. Chem. Res. 25 (1992) 314.
[13] J.P. Collman, V.J. Lee, C.J. Kellenyuen, X.M. Zhang, J.A. Ibers, J.I. Brauman, J. Chem. Soc. 117 (1995) 692.
[14] T.J. Katsuki, Mol. Catal. A 113 (1996) 87.
[15] B. Meunier, Chem. Rev. 92 (1992) 1411.
[16] G. Pratviel, J. Bernadou, B. Meunier, Metal Ions Biol. Syst. 33 (1996) 399.
[17] D.J. Gravert, J.H. Griffin, Metal Ions Biol. Syst. 33 (1996) 515.
[18] G. Christou, Acc. Chem. Res. 22 (1989) 328.
[19] H.H. Thorp, G.W. Brudvig, New J. Chem. 15 (1991) 479.
[20] G.W. Brudvig, H.H. Thorp, R.H. Crabtree, Acc. Chem. Res. 24 (1991) 311.
[21] R. Manchanda, G.W. Brudvig, R.H. Crabtree, Coord. Chem. Rev. 144 (1995) 1.
[22] W. Ruttinger, G.C. Dismukes, Chem. Rev. 97 (1997) 1.
[23] V.L. Pecoraro, M.J. Baldwin, A. Gelasco, Chem. Rev. 94 (1994) 807.
[24] R. Hage, J.E. Uonrg, J. Kerschner, J.H. Koek, E.L.M. Lempers, R.J. Martens, U.S. Racherla, S.W. Russell, T. Swarthoff, M.R.P. van Vliet, J.B. Warnaar, L. van der Wolf, B. Krijner, Nature 369 (1994) 637.
[25] A. Sobkowiak, A. Qui, L. Xiu, A. Llobet, D.T. Sawyer, J. Am. Chem. Soc. 115 (1993) 609.
[26] C. Kang, C. Redman, V. Cepak, D.T. Sawyer, Bioorg. Med. Chem. 1 (1993) 125.
[27] D.T. Sawyer, C. Kang, A. Llobert, C. Redman, J. Am. Chem. Soc. 115 (1993) 5817.
[28] L. Xiu, A. Qiu, D.T. Sawyer, J. Am. Chem. Soc. 115 (1993) 3239.
[29] C. Kang, A. Sobkowiak, D.T. Sawyer, Inorg. Chem. 33 (1994) 79.
[30] D.T. Sawyer, Oxygen Chemistry, Oxford Univ. Press, New York, 1991, p. 85.
[31] A. Sobkowiak, H.C. Tung, D.T. Sawyer, Prog. Inorg. Chem. 40 (1992) 291.
[32] J.P. Hage, J.A. Powell, D.T. Sawyer, J. Am. Chem. Soc. 117 (1995) 12897.
[33] T. Matsushita, L. Spencer, D.T. Sawyer, Inorg. Chem. 27 (1988) 1167.
[34] S.A. Richard, P.K.S. Tsang, D.T. Sawyer, Inorg. Chem. 27 (1988) 1814.
[35] I.M. Kolthoff, E.B. Sandell, E.J. Meehan, S. Bruckenstein, Quantitative Chemical Analysis, 4th edn., MacMillan, New York, 1969, p. 854.