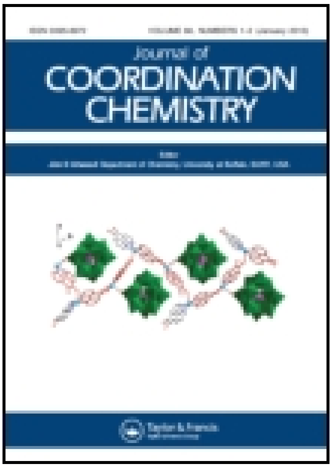

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A water-oxidizing dinuclear iron complex as an efficient catalyst toward organic sulfide oxidation

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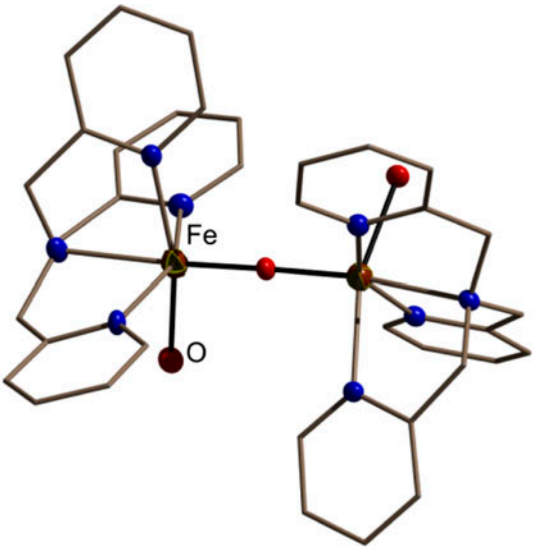

In this paper, we report that a known dinuclear Fe complex, $[tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)_4$ (tpa: tris(2-pyridylmethyl)amine), is an efficient catalyst toward organic sulfide oxidation in the presence of urea-hydrogen peroxide.

Keywords: Dinuclear iron complex; Homogeneous; Oxidation; Sulfide

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1. Introduction

Selective oxidation of organic compounds is an important reaction in the laboratory as well as in chemical industry for producing chemical intermediates to afford useful chemicals [1–7]. Transition metal complexes as catalysts in organic synthesis are extensively employed in a wide range of areas of preparative organic chemistry [8–11].

J.L. Fillol, M. Costas and co-workers reported that mononuclear Fe complexes with neutral tetradentate nitrogen-donor ligands oxidize water with high efficiency, high turnover frequency and number, in the presence of cerium(IV) ammonium nitrate for a period of hours [12]. Different experiments show that the complex is stable and decomposition products are not the catalysts for water oxidation [13–15]. The stability of iron(III) complexes in the presence of cerium(IV) ammonium nitrate is promising for other oxidation reactions. Recently, M.M. Najafpour's group reported a dinuclear iron complex with a tetradentate nitrogen-donor ligand, similar as the one used by Fillol, Costas and co-workers [15]. The catalytic activity of this compound toward water oxidation was even more pronounced than for mononuclear complexes [15]. Here, we used the same dinuclear Fe(III) complex, [tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)$_4$, tpa = tris(2-pyridylmethyl)amine (**1**), to oxidize organic sulfides in the presence of urea-hydrogen peroxide (UHP) [16].

2. *Experimental*

2.1. *General procedure*

Chemicals and solvents were purchased from Fluka and Merck Chemical companies. The products of oxidation reactions were analyzed by an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column and a flame-ionization detector.

2.2. *Synthesis of [tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)$_4$*

The complex was synthesized by a previously reported method [15]: a mixture of tpa·3H-ClO$_4$ (0.2 g, 0.35 mM) and triethylamine (0.12 g, 1.2 mM) dissolved in methanol (7.0 mL) was added to Fe(C1O$_4$)$_3$·6H_2O (0.19 g, 0.4 mM) dissolved in water : methanol (1 : 1, 3 mL) to produce a red solution. Red crystals of **1** were deposited over a few hours. Single crystal of **1** in form of red block was chosen and mounted on a Stoe IPDS2t diffractometer equipped with Mo K_α radiation source to confirm the structure.

2.3. *General procedure for sulfide oxidation*

For sulfide oxidation experiments, we used a standard procedure. To a solution of sulfide (0.2 mM), chlorobenzene (0.2 mM) as an internal standard and [tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)$_4$ (0.005 mM) in a 1 : 1 mixture of CH_3OH/CH_2Cl_2 (1 mL) 0.4 mM UHP was added as an oxidant. The mixture was stirred at room temperature and the reaction progress was monitored by GC. Assignments of the products were made by comparison with authentic samples.

3. Results and discussion

3.1. *Complex characterization*

The identity of the crystalline product was confirmed by X-ray diffraction studies in unit cell constants performed for multiple crystals. In our previous report [15] we undertook a full structure determination of this catalyst, showing it to comprise a [tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)$_4$ perchlorate salt, isomorphous with the reported structure of a different solvate [16]. Structure of the binuclear cation is shown in figure 1 (top). The specific staggered geometry of the H_2O–Fe–O–Fe–OH_2 moiety [figure 1 (bottom)] might be crucial for the catalytic activity, directing a favorable hydrogen bonding pattern. A characteristic feature is shortening of the Fe–O (bridging) bond lengths, thus giving them a partial π-character and limiting the rotation of the terminal ligands bonded to Fe around the Fe–O–Fe axis [17].

3.2. *Catalytic activity*

In order to evaluate the catalytic activities of [tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)$_4$ for oxidation of sulfides, the reactions were optimized with respect to the oxidation of methylphenyl sulfide (**MPS**) through the investigation of solvent, the amount of the catalyst, and the amount of UHP.

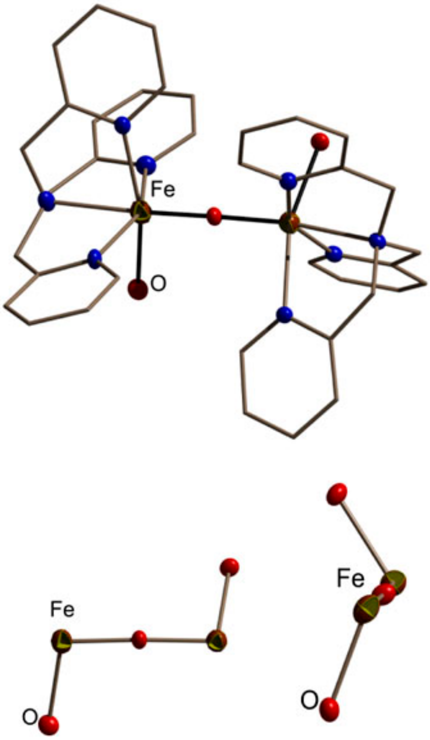


Figure 1. Top: structure of the complex cation in **1** [15] (H atoms omitted); bottom: two views of the staggered Fe(O)–O–Fe(O) moiety.

Dichloromethane, chloroform, acetonitrile, acetone, methanol, and 1 : 1 mixture of CH_3OH/CH_2Cl_2 were employed as solvents in search for optimal conditions. Among the solvents examined, the 1 : 1 mixture of CH_3OH/CH_2Cl_2 was found to be the best for this procedure (table 1). The effect of the amount of the catalyst on the conversion rate and the selectivity of the **MPS** oxidation was also studied (at room temperature for 15 min in CH_2Cl_2/H_2O). The conversion of **MPS** increases monotonously with addition of catalyst from 0 to 0.005 mM (table 1). When the amount of the catalyst is increased to 0.0075 mM, the selectivity of the methylphenylsulfide oxidation reduces from 84 to 75% (table 1, entry 8). Reaction without addition of catalyst proceeds only very slightly. Hence, the amount of the catalyst enhances the reaction rate for selective oxidation of sulfides. The amount of UHP could also significantly affect the selectivity of the conversion to methylphenylsulfoxide (table 1, entries 9–12). When the amount of UHP was increased from 0.1 to 0.4 mM, the conversion of **MPS** increased drastically from 36 to 99%. With a further increase of the amount of UHP to 0.5 mM, the selectivity to methylphenylsulfoxide decreases from 84 to 55%. Selectivity of the conversion to sulfoxide is better for reactions with 2 equiv. of the oxidant when compared to the use of 2.5 equiv. of UHP. The reaction time could also significantly affect the **MPS** conversion and methylphenylsulfoxide selectivity (figure 2). When the time of the reaction was increased from 0 to 15 min, the conversion of **MPS** increased drastically from 0 to 99%. With a further increase of the reaction time to 45 min, the selectivity of conversion to benzaldehyde decreases from 84 to 33%.

After optimization, a series of various types of structurally diverse sulfides were subjected to the oxidation reaction using $[tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)_4$ as a catalyst and UHP as an oxidant. Arylalkyl (table 2, entries 1 and 2), arylbenzyl (table 2, entry 3), dibenzyl (table 2, entry 4), diaryl (table 2, entry 5), and dialkyl (table 2, entries 6–8) sulfides underwent clean and selective oxidation to the corresponding sulfoxide under air, with impressive selectivities (81–93%). Very good conversions of the substrates, depending on the nature of the sulfide, of 71–99% (TON = 28.4–39.6) were obtained in all cases.

Table 1. The effect of various conditions on the oxidation of methylphenylsulfide by $[tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)_4$/UHP.

Entry	Amount of the catalyst (mM)	Amount of UHP (mM)	Solvent (1 mL)	Conversion (%)[a]	Selectivity to sulfoxide (%)[b]
1	0.005	0.4	CH_2Cl_2	17	100
2	0.005	0.4	$CHCl_3$	14	100
3	0.005	0.4	CH_3CN	68	95
4	0.005	0.4	CH_3OH	59	91
5	0.005	0.4	CH_3COCH_3	47	98
6	0.005	0.4	$CH_2Cl_2 : CH_3OH$	99>	84
7	0	0.4	$CH_2Cl_2 : CH_3OH$	Trace	–
8	0.0075	0.4	$CH_2Cl_2 : CH_3OH$	99>	75
9	0.005	0	$CH_2Cl_2 : CH_3OH$	–	–
10	0.005	0.1	$CH_2Cl_2 : CH_3OH$	36	100
11	0.005	0.2	$CH_2Cl_2 : CH_3OH$	58	94
12	0.005	0.3	$CH_2Cl_2 : CH_3OH$	81	90
13	0.005	0.5	$CH_2Cl_2 : CH_3OH$	99>	55

[a] The GC yields (%) are measured relative to the starting sulfide.
[b] Selectivity to sulfoxide = (sulfoxide/(sulfoxide + sulfone)) × 100.

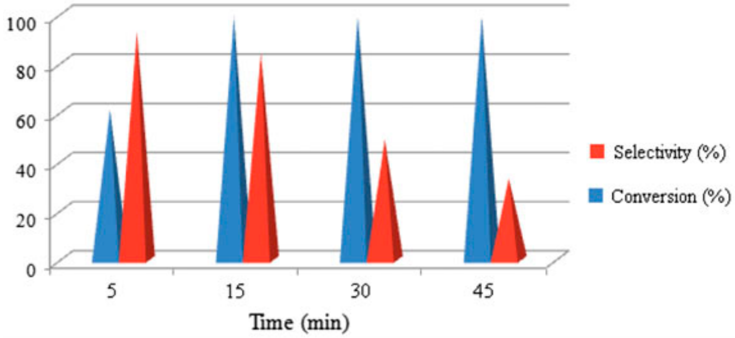
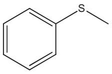
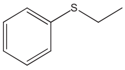
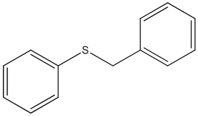
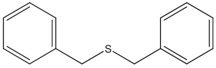
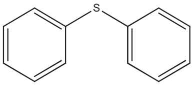
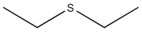
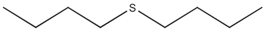
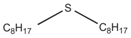


Figure 2. The effect of the reaction time on the MPS oxidation. The molar ratios for [tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)$_4$: substrate : oxidant are 1 : 40 : 80.

It was observed that aromatic sulfides undergo oxidation reactions more easily than the aliphatic substrates. The mechanism of oxidation of organic sulfide by **1** is not known, but it was reported that a very similar dimer undergoes an intramolecular attack by a hydroxide ion coordinated to one Fe center on the carbon of acetonitrile coordinated to the adjacent Fe [scheme 1(a)] [17]. A similar mechanism was proposed for water oxidation catalyzed by this dimer [scheme 1(b)] [15]. In the presence of H_2O_2, reaction of organic sulfide to a Fe=O could be proposed as the mechanism for sulfide oxidation by **1**.

Table 2. Oxidation of sulfides catalyzed by [tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)$_4$ /UHP.[a]

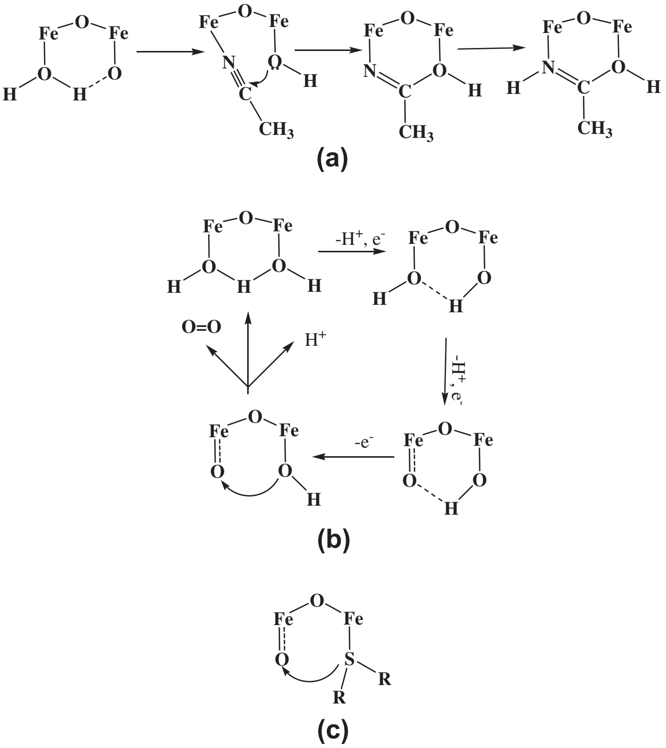
Entry	Substrate	Conversion (%)[b] (TON)[c]	Selectivity (%)[d]
1		99 > (39.6)	84
2		99 > (39.6)	86
3		98(39.2)	88
4		99(39.6)	81
5		85(34)	93
6		73(29.2)	91
7		71(28.4)	90
8		71(28.4)	89

[a]Reaction condition: substrate (0.2 mM), UHP (0.4 mM), [tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)$_4$ (0.005 mM). The reactions were performed in a (1 : 1) mixture of CH_2Cl_2/CH_3OH (1 mL) under air at room temperature within 15 min.

[b]The GC yields (%) are measured relative to the starting sulfide.

[c]TON = (mM of sulfoxide + mM of sulfone)/mM of catalyst.

[d]Selectivity to sulfoxide = (sulfoxide/(sulfoxide + sulfone)) × 100.



Scheme 1. The proposed mechanisms for oxidation of the coordinated acetonitrile (a) [18], water [15] (b) and organic sulfide, (c) catalyzed by **1**.

4. Conclusion

The oxidation of organic sulfides with UHP by a water-oxidizing dinuclear iron complex with high yield and selectivity was reported.

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References

[1] J.A. Schachner, P. Traar, C. Sala, M. Melcher, B.N. Harum, A.F. Sax, M. Volpe, F. Belaj, N.C. Mösch-Zanetti. *Inorg. Chem.*, **51**, 7642 (2012).
[2] M.R. Maurya, S. Dhaka, F. Avecilla. *Polyhedron*, **67**, 145 (2014).
[3] N.-Y. Jin. *J. Coord. Chem.*, **65**, 4013 (2012).
[4] M. Bagherzadeh, M. Zare. *J. Coord. Chem.*, **66**, 2885 (2013).
[5] M. Bagherzadeh, M.M. Haghdoost, F.M. Moghaddam, B.K. Foroushani, S. Saryazdi, E. Payab. *J. Coord. Chem.*, **66**, 3025 (2013).

[6] R. Maurya, M. Kumar, S. Sikarwar. *React. Funct. Polym.*, **66**, 808 (2006).
[7] M. Amini, A. Arab, R. Soleyman, A. Ellern, L.K. Woo. *J. Coord. Chem.*, **66**, 3770 (2013).
[8] S. Pasayat, S.P. Dash, S. Roy, R. Dinda, M.R. Maurya, W. Kaminsky, Y.P. Patil, M. Nethaji, S. Dhaka. *Polyhedron*, **67**, 1 (2014).
[9] M. Amini, M. Bagherzadeh, Z. Moradi-Shoeili, D.M. Boghaei, A. Ellern, L.K. Woo. *J. Coord. Chem.*, **66**, 464 (2013).
[10] M. Bagherzadeh, M.M. Haghdoost, A. Shahbazirad. *J. Coord. Chem.*, **65**, 591 (2012).
[11] M. Amini, M. Bagherzadeh, B. Eftekhari-Sis, A. Ellern, L.K. Woo. *J. Coord. Chem.*, **66**, 1897 (2013).
[12] J.L. Fillol, Z. Codolà, I. Garcia-Bosch, L. Gómez, J.J. Pla, M. Costas. *Nature Chem.*, **3**, 807 (2011).
[13] D. Hong, S. Mandal, Y. Yamada, Y. Lee, W. Nam, A. Llobet, S. Fukuzumi. *Inorg. Chem.*, **52**, 9522 (2013).
[14] G. Chen, L. Chen, S.M. Ng, W.L. Man, T.C. Lau. *Angew. Chem., Int. Ed.*, **52**, 1789 (2013).
[15] M.M. Najafpour, A.N. Moghaddam, D.J. Sedigh, M. Hołyńska, *Catal. Sci. Technol.*, **4**, 30 (2014).
[16] B.R. Whittlesey, Z. Pang, R.A. Holwerda. *Inorg. Chim. Acta*, **284**, 124 (1999).
[17] K.S. Murray. *Coord. Chem. Rev.*, **12**, 1 (1974).
[18] A. Hazell, K.B. Jensen, C.J. McKenzie, H. Toftlund. *Inorg. Chem.*, **33**, 3127 (1994).