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AEROBIC OXIDATION OF SOME ARYLTHIOLS CATALYZED BY A NEW MANGANESE (III) SCHIFF-BASE COMPLEX

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Bis(2-hydroxybenzene)phthaldimine (BHBPDI) as a new quadridentate Schiff base ligand and its $[Mn^{(III)}(BHBPDI)Cl]$ complex were synthesized and characterized by analytical and spectral data (MS, FT-IR, UV-Vis, 1H NMR). The aerobic oxidation of thiols catalyzed by $Mn^{(III)}$ -complex using molecular oxygen was studied at room temperature. The reaction proceeded to yield the corresponding symmetric disulfides in good to high yields. The reaction was retarded when the reaction mixture was saturated with nitrogen gas. This system provides an efficient and convenient method for the oxidation of thiols to symmetric disulfides.

Keywords Air; disulfides; $Mn(III)$; oxidation; Schiff-base complex; thiols

INTRODUCTION

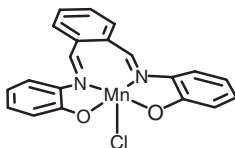
The oxidation of thiols is the most exploited method for disulfide synthesis, mainly because a large number of thiols are commercially available and/or are easily synthesized. The oxidation of thiols to the corresponding disulfides is also of interest from a biological point of view.^{1–2} Thiols are among functional groups that can be easily over-oxidized and, therefore, extensive studies have been carried out to develop controlled conditions to prevent this from occurring. Various reagents or catalytic systems such as permanganates,³ tungstated or molybdated sulfuric acid/ $NaNO_2$,⁴ transition metal catalysts such as Schiff base and porphyrin complexes,⁵ sodium perborate,⁶ ferric chloride,⁷ sodium chlorite,⁸ nitric oxide,⁹ hydrogen peroxide¹⁰ and halogens,¹¹ 2,6-dicarboxypyridinium chlorochromate,¹² monochloro poly(styrenediydantoin) beads,¹³ *N*-phenyltriazolinedione,¹⁴ and sulfonyl chloride¹⁵ among others have been utilized for the oxidation of thiols. Enzymatic¹⁶ and electrochemical¹⁷ methods are also known to perform this oxidative transformation. Most of the reported methods suffer from disadvantages such as expensive, rare, or toxic reagents. However, recent demands for environmentally friendly chemical reactions have encouraged chemists to develop clean and inexpensive reactions for the oxidation of thiols.^{18–20} Thus a simple, mild, clean, and efficient oxidative method to oxidation of thiols to disulfide is still needed. In this direction, molecular oxygen is a candidate for a green oxidant due to its strength and lack of toxic byproducts. There are only rare reports on aerobic oxidation

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of thiols to disulfides.^{21–23} In continuation of our current studies in the selective oxidation of thiols,^{4,5} we wish to report a very efficient and simple method for catalytic oxidative coupling of some aryl thiols into the corresponding disulfides using molecular oxygen using a new Mn(III) Schiff-base complex $[\text{Mn}^{\text{(III)}}(\text{BHBPDl})\text{Cl}]$ as catalyst (**1**) (Scheme 1) including a new quadridentate ligand, bis(2-hydroxybenzene)-phthalaldimine (BHBPDl), under mild conditions.



Scheme 1 Structure of $[\text{Mn}^{\text{(III)}}(\text{BHBPDl})\text{Cl}]$ complex (**1**).

RESULTS AND DISCUSSION

The ligand was prepared based on common method, by condensation of a 1:2 molar ratio of phthaldialdehyde and 2-aminophenol in ethanol under reflux. Elemental analysis, MS, FT-IR, and ^1H NMR confirmed the synthesis of ligand. The mass spectrum of the ligand shows some main peaks at 318 ($\text{M}^+ + 2$), 314 ($\text{M}^+ - 2$), 298 ($\text{M}^+ - \text{OH}$), 282 ($\text{M}^+ - 2\text{OH}$), 223 ($\text{M} - \text{HOC}_6\text{H}_4$) that confirm the molecular structure of the ligand. The IR spectral data of BHBPDl using KBr pellets are in agreement with the structure. The broad absorption band centered at around 3306 cm^{-1} is readily ascribed to the O—H stretching. The absorption band at 1634 cm^{-1} is due to the $-\text{C}=\text{N}$ stretching of the ligand that is appeared at lower frequency than that for $-\text{C}=\text{O}$ stretching (1686 cm^{-1}) of phthaldialdehyde as starting material. Also, elimination of two sharp absorption bands in 3375 and 3304 cm^{-1} and a very broad one centered in 2851 cm^{-1} , as the characteristic bands of $-\text{NH}_2$ and $-\text{OH}$ of 2-aminophenol as starting amine, are in good agreement with the molecular structure. The solution NMR data of the BHBPDl also confirm the structure of the ligand. The ^1H NMR spectrum recorded in $\text{DMSO}-d_6$ solution shows two broad singlets at 10.22 and 8.88 ppm for two OH groups of the ligand, probably because one of them has been involved in the intramolecular hydrogen bonding $[\text{O}-\text{H} \cdots \text{N}]$ in a stable conformer in the solution. The ^1H NMR spectrum also exhibits the expected peaks at 7.57 (m, 4H) for phthalaldimine ring and 7.16 (m, 2H, $-\text{CH}=\text{N}$), 6.93 (m, 2H), 6.61 (m, 2H), and 6.35 (m, 4H) ppm for two aminophenol aromatic rings of the ligand. The synthesis of $[\text{Mn}^{\text{(III)}}(\text{BHBPDl})\text{Cl}]$ was similar to the experimental procedure reported previously in the literature.^{24,26} Elemental analysis, IR spectra, and conductivity resulted in satisfactory data. The absorption band at 1653 cm^{-1} , which can be assigned to the coordinated $-\text{C}=\text{N}$ stretching, is a characteristic band of the complex (**1**). The conductivity measurement in methanol indicates that the Mn(III) complex is neutral ($\Omega = 20.57\text{ }\mu\text{S/cm}$).^{25,26} During our investigations on the development of organic transformations utilizing Schiff base complexes as catalysts under aerobic or non-aerobic conditions, we found that 4-bromothiophenol was oxidized under aerobic conditions effectively in the presence of $[\text{Mn}^{\text{(III)}}(\text{BHBPDl})\text{Cl}]$ as catalyst (**1**). Therefore, this compound was selected as a typical substrate for the optimization of the conditions. At first, we investigated various solvents to run this conversion. As shown in Figure 1, ethanol was found to be the most effective solvent for this oxidation.

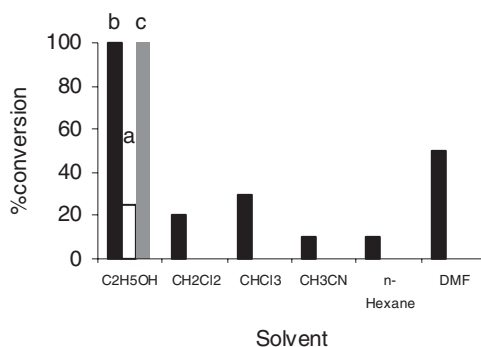
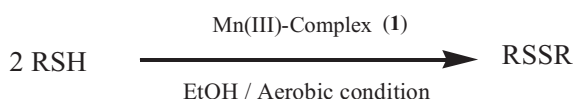


Figure 1 The solvent effect on the aerobic oxidative coupling of 4-bromothiophenol after 1 h using 10% mol of catalyst (**1**). The labels of a, b, and c refer to the percent conversion at three temperatures of 0°C, room temperature, and 40°C in ethanol after 60, 60, and 50 minutes, respectively.

Figure 1 also shows the performance of the reaction at 0°C, room temperature, and 40°C in ethanol. At 0°C, the conversion was decreased (25% conversion), whereas the selectivity was reduced significantly at elevated temperature more than room temperature, and several unidentified byproducts were formed. Further, when the oxidative coupling of 4-bromothiophenol was done using different amounts of catalyst (**1**), the reaction was found to be completed in shorter reaction time with increase in mole percent of catalyst (**1**) up to 10%. The oxidation reaction did not occur at the same condition in the absence of catalyst (**1**) (Figure 2) and/or when using the ordinary Mn(III) salt such as Mn(III) acetate as the catalyst, even after prolonged reaction time. To confirm the role of the molecular oxygen as an oxidant in this reaction, two parallel reactions were designed so that in one reaction, the air is bubbled and in the other, nitrogen gas is bubbled. Under nitrogen, oxidative coupling of thiols did not occur. This observation refers to the key role of molecular oxygen in this reaction (Scheme 2).



Scheme 2 Oxidative coupling of thiols.

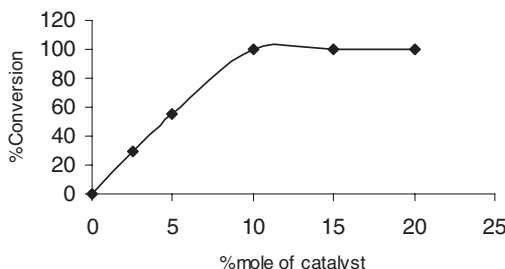
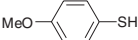
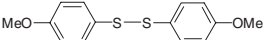
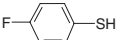
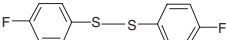

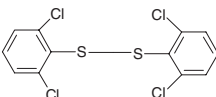
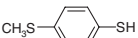
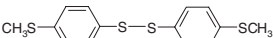
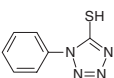
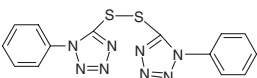
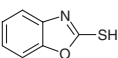
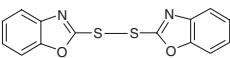
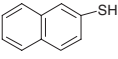
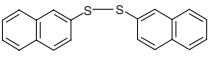

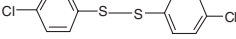

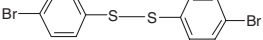
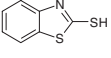
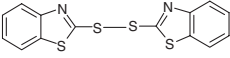

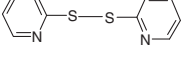

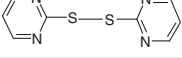


Figure 2 The effect of mole% of Mn(III) complex (**1**) on the aerobic oxidative coupling of 4-bromothiophenol after 1 h.

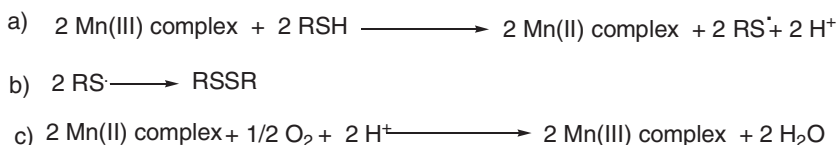
Table I Aerobic oxidation of thiols to the corresponding disulfides catalyzed by [Mn^(III)(BHPDI)Cl] (**1**) in ethanol at room temperature

Entry	Thiol	Disulfide ^a	Time (h)	Yield ^b (%)	Mp (°C) [Lit.]
1			5	90	78–80 ²⁷
2			2.9	89	Oil ²⁷
3			4	92	80–83 ⁵
4			3.58	94	40–43 ^{5,26}
5			4.5	90	58–60 ²⁷
6			3	85	200–201 ²⁷
7			1	94	145–147 ^{5,27}
8			1	91	72–73 ^{5,27}
9			1	93	90–92 ²⁷
10			2.8	90	177–179 ⁵
11			1.75	95	55–56 ⁵
12			1.66	90	133–135 ^{5,27}

^aIdentified by physical, spectral data, and comparison with those reported in the literature.^bRefers to isolated yields.

Finally, the oxidative coupling of a variety of thiols was examined using the optimized reaction conditions, and oxidation was observed in high yields during 1–5 h of reactions (Scheme 1 and Table I). When an ethanolic solution of Mn(III) complex in aerated conditions was treated with a typical thiol, the initial dark brown color changed to a light brown solution. Based on the literature, the dark brown and light brown solutions of catalyst (**1**) refer to Mn(III) and Mn(II) complexes, respectively.²² With regard to the literature and our observations, the proposed reaction mechanism is as shown in Scheme 3. The Mn(III) complex oxidizes the thiol molecules to thionyl radicals and is itself reduced to Mn(II) complex. Thionyl radicals are coupled to give the related disulfides. Then the Mn(III) complex is regenerated by treatment with molecular oxygen and entered to the next cycle of oxidation.

As shown in Table I and with regard to mechanism of Scheme 3, the thiols including electronegative substituents, especially in 2-positions (Table I, entries 1, 2, 3, and 4) are oxidized slower than others due to the instability of thionyl radicals and steric effect,



Scheme 3 Proposed reaction mechanism for oxidative coupling of thiols.

respectively. The thiols with heterocyclic rings (Table I, entries 5, 6, 10, 11, and 12) are oxidized at the next preference, which is related to thiol-thione equilibriums of them in solution that make them difficult to be oxidized. The thiols of entries of 7, 8, and 9 are oxidized in shorter times with respect to others because of facility of oxidation due to relative stability of produced thionyl radicals. Tenfold scale oxidation of 4-bromothiophenol (10 mmol) was also carried out. The results showed that oxidation took place in good yield (less than 5% yield was lost). Reusability of catalyst was investigated by the use of it in three sequential reactions that resulted in no efficient loss of catalytic activity (10% yield was lost after the third use of it). Catalyst stability has been investigated by FT-IR and UV-visible spectroscopy. The spectral data confirmed that the structure of the complex is stable during the reactions.

EXPERIMENTAL

Chemicals were obtained from Merck or Fluka and used without further purification. The reactions were monitored by TLC (silica-gel 60 F254, *n*-hexane:ethylacetate, 15:5). The electronic absorption spectra were recorded with a Jasco UV-570 spectrophotometer. ^1H NMR spectra were obtained with a Bruker DPX-250 and/or 500 MHz spectrometer. Mass spectra were recorded on an AMD 604 spectrometer, EI-mode at 70 eV, FT-mode at 0.005 V and/or Shimadzu model GC-MS QP5050. IR spectra were recorded on a FT-IR Jasco-680 spectrophotometer. Molar conductivity of the complexes was measured by Metrohm 712 model. Elemental analyses (CNHS) of samples were performed using a CHNS-932 elemental analyzer by the central instrumental laboratory of Tarbiat Moallem University of Tehran.

Preparation of the Ligand, Bis(2-Hydroxybenzene)phthaldimine (BHBPDI)

To a ethanolic solution (25 mL) of 2-aminophenol (0.546 g, 5 mmol), phthaldialdehyde (0.335 g, 2.5 mmol) in 25 mL ethanol was gradually added, and the reaction mixture was refluxed. The progress of the reaction was monitored by TLC. After 8 h, cooled water (50 mL) was added to the reaction mixture to form a deep yellow precipitate that was filtered, washed with water and ethanol/water mixture (15 mL) twice, and finally recrystallized from ethanol. The 1,2-bis(2-hydroxybenzene)phthaldimine was obtained in 76% yield. Mp = 117–120 °C. Elemental anal. calcd. (%) $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$: C 48.93, H 4.62; N 7.13. Found: C 49.27, H 4.72, N 6.96. IR (KBr, cm^{-1}): 3306 (bs, νOH), 3061 (w, CH-Aromatic), 2976 (w, CH-imine), 1634 (vs, $\nu\text{C}=\text{N}$ -imine), 1493 (s), 1586 (s), 1453 (s, $\nu\text{C}=\text{C}$, aromatic ring), 1331 (m), 1302 (m), 1274 (m), 1209 (m, $\nu\text{C}-\text{N}$), 1146 (m), 1123 (w), 1033 (m, C—O), 928 (w), 896 (m), 747 (s), 727 (s), 657 (m), 566 (w), 471 (m). UV (CH_2Cl_2), λ_{max} : 223 and 306 nm. ^1H NMR ($\text{DMSO}-d_6$, ppm): 10.22 (bs, 1H), 8.88 (bs,

1H), 7.57 (m, 4H, phthaldimine benzene ring), 7.16 (m, 2H, CH=N), 6.93 (m, 2H), 6.61 (m, 2H) and 6.35 (m, 4H). Mass (m/z): 318 ($M^+ + 2$), 314 ($M^+ - 2$), 298 ($M^+ - OH$), 282 ($M^+ - OH$), 223 ($M - HOC_6H_4$), 209, 196, 186, 168, 150, 129, 122, 113, 97, 93, 79, 77, 64, 51.

Preparation of [Mn(BHBPDl)Cl] Complex as the Catalyst

Manganese insertion into BHBPDl was achieved by heating the free-base BHBPDl (1.58 g, 5 mmol) and $MnCl_2 \cdot 4H_2O$ (0.989 g, 5 mmol), respectively, in a similar method to that reported in literature,^{7,10,24,26} under reflux and aerobic conditions, in ethanol (50 mL), for 4–6 h. After cooling, the solids were collected by filtration and washed twice with a small portion of ethanol (10 mL) and then recrystallized from a water/ethanol mixture to give 68% yield of product. Elemental analysis calculated for $[Mn^{(III)}(BHBPDl)Cl] \cdot H_2O$, $\{C_{20}H_{16}ClMnN_2O_3\}$, (%): C, 56.82; H, 3.81; N, 6.63; Found: C 56.47, H 4.06, N 6.86. Mp ($^{\circ}C$) = ($>340^{\circ}C$, dec.): IR (KBr, cm^{-1}): 3276(m, $\nu(H_2O)$), 3063, 1654, (s, $\nu(-C=N)$), 1593, 1496, 1453, 1243, 1200, 1036, 851, 814, 745, 704, 584, 476. UV(CH_2Cl_2), λ_{max} : 223, 300 and 431 nm. Molar conductivity in methanol is $\Omega = 20.57 \mu S/cm$.

Aerobic Oxidation of Thiols Catalyzed by $[Mn^{(III)}(BHBPDl)Cl]$

To the Mn(III) complex (0.1 mmol, 10% molar ratio) in methanol (20 mL), the thiol (1 mmol) was added, and then the solution was aerated. The reaction mixture was stirred at room temperature until TLC indicated the reaction was completed. The resulting solution was concentrated under reduced pressure to yield a residue, which was passed through a short pad of silica gel using ethyl acetate and hexane (1:2) as eluent to provide analytically pure product in good to high yields. All products are known, and their physical and spectral data were compared with those reported in the literature. The results are summarized in Table I.

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