Synthesis, X-ray Studies, and Catalytic Efficacy of a Novel Iron Complex Containing an N,O-Type Bidentate Thiazoline Ligand

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Abstract. The reactions of FeCl₃·6H₂O and 2-(2'-hydroxyphenyl)-2thiazoline as a bidentate O-N donor thiazoline ligand (thoz) afford a five-coordinate Fe^{III} complex [Fe(thoz)₂Cl] with a distorted square pyramidal configuration. Complex [Fe(thoz)₂Cl] was isolated as airstable crystalline solids and fully characterized, including by single-

Introduction

Model compounds play a significant role in establishing the structure of enzymic intermediates and contribute to a better understanding of their catalytic properties and behavior.^[1,2] Iron is the most prominent transition metal in biological perspective, as many enzymes containing ferrous or ferric ion catalyze various bio-transformations. Therefore a growing interest in the coordination chemistry of iron is based on the recognition of its importance from a biological, pharmacological, and catalytic perspective.^[3,4]

Multidonor ligands containing nitrogen and sulfur atoms, and their versatile chelating ability with transition metal ions, have attracted considerable interest in a wide range of asymmetric catalytic reactions.^[5–9] Among these ligands, 2-(2'-hydroxyphenyl)-2-thiazoline (Hthoz), found in the microbial in the iron chelator (*S*)-(–)-desferrithiocin. Several metal complexes bearing 2-(2'-hydroxyphenyl)-2-thiazoline have been reported in the literature.^[10,11]

The oxidation of sulfides to sulfoxides is of significant importance in organic chemistry, both for fundamental research and for a wide range of applications.^[12–14] Organic sulfoxides are useful synthetic intermediates for the construction of various chemically and biologically active molecules since then, a number of methods have been developed for the conversion of sulfides into sulfoxides.^[15,16] In particular, iron would be an ideal candidate to be an environmentally benign catalyst because of its easy availability, low toxicity, and low price as

Iowa State University Iowa 50011–3111, USA crystal X-ray structure analysis. Complex $[Fe(thoz)_2Cl]$ shows very efficient reactivity in the oxidation of sulfides to their corresponding sulfoxides using urea hydrogen peroxide (UHP) as the oxidant at room temperature in air.

well as exceptional catalytic activity and in recent years, significant advances in the oxidation of sulfides has been accomplished by applying iron catalysts.^[17–20]

We recently reported highly efficient method for the oxidation of sulfides by using of a Fe^{III} complex with 2-(2'-hydroxyphenyl)-5,6-dihydro-1,3-oxazine as oxazine ligand.^[21] In order to study the effect of the ligand on the catalytic reactivity, herein we describe the synthesis of a new Fe^{III} complex [Fe(thoz)₂Cl] [Hthoz = 2-(2'-hydroxyphenyl)-2-thiazoline] and the use of this complex as a catalyst in the oxidation of sulfides in the presence of urea hydrogen peroxide (UHP) as an oxidant in an air atmosphere at room temperature (Scheme 1). This is the first report on the catalytic activity of a thiazoline-Fe^{III} complex in oxidation reactions.

$$R-S-R' \xrightarrow{[Fe(thoz)_2Cl], UHP} R-S-R' + R-S-R' + R-S-R'$$

Scheme 1. The oxidation of sulfides by the $[Fe(thoz)_2Cl]/UHP$ catalytic system.

Results and Discussion

Complex Characterization

The complex was obtained by the reaction of 2 equiv. of the ligand 2-(2'-hydroxyphenyl)-2-thiazoline and FeCl₃·6H₂O (Scheme 2). The fast color change from a pale yellow to a dark



Scheme 2. Synthesis of the complex [Fe(thoz)₂Cl].

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Figure 1. ORTEP diagram of the complex [Fe(thoz)₂Cl] with thermal ellipsoids are drawn at a 50% probability limit.

brown solution during the synthesis indicated the coordination of ligand.

The elemental analyses and spectroscopic data confirm the assigned composition of the complex [Fe(thoz)₂Cl]. The IR spectra of the complex clearly showed the coordination of the ligands, as exemplified by the shift of the absorption band assigned to C=N bonds from 1624 (free ligand) to 1611 cm⁻¹ (iron complex).^[21–23]

Also the structure of the complex was determined by X-ray crystallography and an ORTEP view of the complex with atom numbering scheme is shown in Figure 1. The summary of single-crystal X-ray structure refinement is shown in Table 1. The five-coordinate iron(III) complex crystallize in the triclinic crystal system and space group $P\overline{1}$. In the crystal structure of [Fe(thoz)₂Cl] the weak intermolecular C–H···Cl interactions connect the molecules throughout the lattice (Figure 2).

The structure shows that the two ligands are coordinated to iron in the expected bidentate fashion through oxygen and nitrogen atoms. This complex consists of the distorted square pyramidal Fe^{III} unit with two nitrogen atoms and two oxygen atoms of two deprotonated ligand, 2-(2'-hydroxyphenyl)-2-thiazoline, occupying the basal plane [Fe–N distances 2.0935(13) Å and 2.1028(13); Fe–O distances 1.8736(11) and 1.8870(12) Å] and the chloride ion in the apical position with the significantly longer bond length of 2.2576(5) Å.

Catalytic Activity

In order to evaluate the catalytic activities of complex $[Fe(thoz)_2Cl]$ for the oxidation of sulfides, the reactions were optimized according to the oxidation of methylphenyl sulfide through the investigation of the influence factors of the oxidation, such as the solvent, the amount of the catalyst and the amount of the UHP.

Table 1. Crystal data and structure refinement for complex $[Fe(thoz)_2Cl]$.

| | Fe(thoz) ₂ Cl |
|--|--|
| Empirical formula | C ₁₈ H ₁₆ ClFeN ₂ O ₂ S ₂ |
| Formula weight | 447.75 |
| Temperature /K | 173(2) |
| Wavelength /Å | 0.71073 |
| Crystal system | triclinic |
| Space group | PĪ |
| Unit cell dimensions | a = 8.2324(12) Å |
| | $a = 90.055(2)^{\circ}$ |
| | b = 9.6609(14) Å |
| | $\beta = 98.540(2)^{\circ}$ |
| | c = 12.2752(17) Å |
| | $\gamma = 107.110(2)^{\circ}$ |
| Volume /Å ³ | 921.7(2) |
| Ζ | 2 |
| Density (calculated) /Mg·cm ⁻³ | 1.613 |
| Absorption coefficient /mm ⁻¹ | 1.205 |
| F(000) | 458 |
| Crystal size /mm | $0.08 \times 0.26 \times 0.26$ |
| Theta range for data collection /° | 1.68 to 28.81 |
| Index ranges | $-11 \le h \le 11$ |
| | $-13 \le k \le 13$ |
| | $-16 \le l \le 16$ |
| Reflections collected | 9963 |
| Independent reflections | 4756 [R(int) = 0.0174] |
| Completeness to $\theta = 28.70^{\circ}$ | 98.6% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9098 and 0.7447 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 4756 / 0 / 235 |
| Goodness-of-fit on F^2 | 1.041 |
| Final <i>R</i> indices $[I > 2\sigma(I)]^{a}$ | $R_1 = 0.0265, wR_2 = 0.0676$ |
| <i>R</i> indices (all data) ^{a)} | $R_1 = 0.0308, wR_2 = 0.0699$ |
| Largest diff. peak and hole /e·A ⁻³ | 0.456 and -0.251 |

a) $R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma [F_o^2]$. $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma ||F_o|$. GOOF = $S = \{\Sigma [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$. $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$. $w = 1 / [\sigma(F_o^2) + (aP)^2 + bP]$ where P is $[2F_c^2 + Max(F_o^2, 0)] / 3$.





Figure 2. Depicting weak intermolecular C–H···Cl interactions bonded 1D polymeric array along *a* axis for complex [Fe(thoz)₂Cl].

For finding the best solvent for the sulfide oxidation, dichloromethane, chloroform, acetonitrile, acetone, methanol and a 1:1 mixture of CH_3OH/CH_2Cl_2 were employed as solvents. Among the solvents examined, the 1:1 mixture of $CH_3OH/$ CH_2Cl_2 was found to be the best for this protocol (Table 2). The effect of amount of catalyst on the conversion and the selectivity of the methylphenylsulfide oxidation at room temperature for 15 min in CH_2Cl_2/H_2O was also studied. The conversion of methylphenylsulfide monotonously increases with the addition of catalyst of 0 to 0.01 mmol (Table 2). When the amount of catalyst is increased to 0.015 mmol, the selectivity of the methylphenylsulfide oxidation is reduced from 86 to 71% (Table 2, entry 9). The reaction without catalyst is found to proceed only very slightly. Hence, the amount of catalyst can enhance the reaction rate for the selective oxidation of sulfides. The amount of UHP could also significantly affect the conversion and methylphenylsulfoxide selectivity (Table 2, entries 10-13). When the amount of UHP was increased from 0.1 to 0.4 mmol, the conversion of methylphenylsulfide was drastically increased from 26 to 91%. With a further increase of UHP to 0.5 mmol, the selectivity to methylphenylsulfoxide decreases from 86 to 65%, where the conversion of methylphenylsulfide was also increased from 91 to 99%. In other words selectivity to sulfoxide would appear to be better for reactions with 2 equiv. of the oxidant compared to this with 2.5 equiv. of UHP. Also, when UHP was replaced with H_2O_2 , the activity towards the oxidation of methylphenylsulfide was decreased from 91 to 68%.

After optimization, a series of various types of structurally diverse sulfides was subjected to the oxidation reaction using the complex [Fe(thoz)₂Cl] as catalyst and UHP as oxidant. Arylalkyl (Table 3, entries 1,2), arylbenzyl (Table 3, entry 3), dibenzyl (Table 3, entry 4), diaryl (Table 3, entry 5), and dialkyl (Table 3, entries 6-8) sulfides underwent clean and selective oxidation to the corresponding sulfoxide in air in impressive selectivity (81-100%). Significantly, the very good conversions of substrates, depending on the nature of the sulfide in the range of 49-97% (TON = 11.4-18.2), were obtained for all cases. It was observed that aromatic sulfides undergo oxidation reactions more easily than aliphatic substrates. Moreover in the case of dialkyl sulfides (Table 3, entries 6-8), no over-oxidation to sulfone was observed. The highest and the lowest conversions were obtained for dibenzyl sulfide (97%) and dioctyl sulfide (49%), respectively (Table 3, entries 4,8).

In order to show the merit and efficiency of the present catalytic system in comparison with recently reported protocols, we compared the results of the methylphenyl sulfide oxidation

Table 2. The effect of various conditions in the oxidation of methylphenylsulfide by [Fe(thoz)₂Cl]/UHP.

| Entry | Amount of catalyst /mmol | Amount of UHP /mmol | Solvent /1 mL | Conversion /% (TON) ^{a)} | Selectivity to sulfoxide b) /% |
|-------|--------------------------|---------------------|---|-----------------------------------|--------------------------------|
| 1 | 0.005 | 0.4 | CH ₂ Cl ₂ | 5(2) | 100 |
| 2 | 0.005 | 0.4 | CHCl ₃ | 11(4.4) | 100 |
| 3 | 0.005 | 0.4 | CH ₃ CN | 22(8.8) | 100 |
| 4 | 0.005 | 0.4 | CH ₃ OH | 47(18.8) | 99 |
| 5 | 0.005 | 0.4 | CH ₃ COCH ₃ | 35(15) | 100 |
| 6 | 0.005 | 0.4 | CH ₂ Cl ₂ :CH ₃ OH | 71(28.4) | 97 |
| 7 | 0 | 0.4 | CH ₂ Cl ₂ :CH ₃ OH | trace | _ |
| 8 | 0.01 | 0.4 | CH ₂ Cl ₂ :CH ₃ OH | 91(18.2) | 86 |
| 9 | 0.015 | 0.4 | CH ₂ Cl ₂ :CH ₃ OH | 93(12.4) | 71 |
| 10 | 0.01 | 0.1 | CH ₂ Cl ₂ :CH ₃ OH | 26(5.2) | 100 |
| 11 | 0.01 | 0.2 | CH ₂ Cl ₂ :CH ₃ OH | 43(8.6) | 98 |
| 12 | 0.01 | 0.3 | CH ₂ Cl ₂ :CH ₃ OH | 68(13.6) | 94 |
| 13 | 0.01 | 0.5 | CH ₂ Cl ₂ :CH ₃ OH | 99(19.8) | 65 |
| 14 | 0.01 | 0.4 ^{c)} | CH ₂ Cl ₂ :CH ₃ OH | 68 (13.6) | 96 |

a) TON = (mmol of sulfoxide + mmol of sulfone)/mmol of catalyst. b) Selectivity to sulfoxide = $[sulfoxide\% / (sulfoxide\% + sulfone\%)] \times 100$. c) H₂O₂ as oxidant.

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Table 3. Oxidation of sulfides catalyzed by [Fe(thoz)₂Cl]/UHP ^{a)}.

| Entry | Substrate | Conversion (%) ^[b] (TON) ^[c] | Selectivity (%) ^[d] |
|-------|-----------------|---|-----------------------------------|
| 1 | s_ | 91(18.2) | 86 |
| 2 | | 87(17.4) | 85 |
| 3 | | 95(19) | 88 |
| 4 (| | 97(19.4) | 81 |
| 5 | | 82(16.4) | 88 |
| 6 | S S | 61(12.2) | 100 |
| 7 | \sim | 55(11) | 100 |
| 8 | Coller S Coller | 49(9.8) | 100 |

in the presence of iron catalysts. As shown in Table 4, our catalytic system is superior to some of the previously reported catalysts in terms of reaction conditions, conversion, and selectivity. In contrast to similar, previously reported systems, the catalytic system presented in this paper does not suffer from the harsh reaction conditions, such as using large amounts of hazardous solvents (Table 4, entries 2 and 4), high reaction temperature (Table 4, entry 3), long reaction time (Table 4, entries 3–5) and using an additive (Table 4, entry 4). As illustrated in Table 4, both Fe^{III} complexes [Fe(thoz)₂Cl] and [Fe(N–O)₂Cl] (Table 4, entry 6) are almost equally effective sulfide oxidation catalysts.

Conclusions

a) The molar ratios for [Fe(thoz)₂Cl]:substrate:oxidant are 1:20:40. The reactions were performed in a 1:1 mixture of CH₂Cl₂/CH₃OH (1 mL) in air at room temperature within 15 min. b) The GC yields /% are measured relative to the starting sulphide. c) TON = (mmol of sulfoxide + mmol of sulfone)/mmol of catalyst. d) Selectivity to sulfoxide = [sulfoxide%/(sulfoxide% + sulfone%)] × 100.

The novel five-coordinate Fe^{III} complex [Fe(thoz)₂Cl] was synthesized and characterized by physico-chemical methods. X-ray diffraction studies revealed the coordination of the bidentate thiazoline ligand 2-(2'-hydroxyphenyl)-2-thiazoline to the iron in a chelate way by oxygen and nitrogen atoms. The solid state studies further exemplified the distorted square pyramidal configuration around the iron atom. In this study we have demonstrated the effectiveness of this complex as a catalyst for the oxidation of sulfides to their corresponding

Table 4. Recently reported catalytic systems for the oxidation of sulfides by iron catalysts.

| Entry | Catalyst | Conditions | Conversion (%) | Selectivity to sulfoxide (%) ^[a] | Time (min) | Ref. |
|-------|------------------|---|-------------------|--|---------------|-----------------|
| 1 | | The molar ratios for catalyst: substrate: UHP are 1:20:40; (CH ₂ Cl ₂ :CH ₃ OH (1 mL) at room temperature). | 91 | 86 | 15 | Present work |
| 2 | | The molar ratios for catalyst: substrate: H_2O_2 are 1:25:25; (CH ₃ CN (5mL) at room temperature). | 94 | | <u>a</u> r | [17] |
| 3 | | The molar ratios for catalyst: substrate are 1:50; (O ₂ (2MPa) PEG-1000 (0.3 g), at 100 °C). | 100 | 94 | 120 | [18] |
| 4 | N Ph Ph Cl | The molar ratios for catalyst: substrate are 1:60:50; (anisic acide (10 equiv) as an additive, CH_3CN (4mL) at room temperature). | 85 | 93 | 60 | [19] |
| 5 | | The molar ratios for catalyst: sulfide: UHP are 1:20:40; (CH ₂ Cl ₂ :CH ₃ OH (1mL)). | 54 | 89 | 30 | [20] |
| 6 | | The molar ratios for catalyst: substrate: UHP are 1:20:40; (CH ₂ Cl ₂ :CH ₃ OH (1mL)). | 85 | 86 | 15 | [21] |

a) Selectivity to sulfoxide = $[sulfoxide\%/(sulfoxide\% + sulfone\%)] \times 100$.



sulfoxides. Easy preparation, mild reaction condition, the use of UHP as green oxidant, high yields of the products, short reaction time, low over-oxidation to sulfones (0–18%), high selectivity, and low cost make [Fe(thoz)₂Cl]/UHP as a useful catalytic system for the oxidation of sulfides.

Experimental Section

General Procedures: Chemicals and solvents were purchased from the Fluka and Merck Chemical companies. The elemental analysis (carbon, hydrogen, and nitrogen) of the compound was obtained with a Carlo ERBA Model EA 1108 analyzer. FT-IR spectrum was obtained with a Unicam Matson 1000 FT-IR spectrophotometer using KBr disks at room temperature. MS spectra were recorded with a Finnigan MAT95 spectrometer. The products of oxidation reactions were determined and analyzed with an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column and a flame-ionization detector. The crystal evaluation and data collection were performed with a Bruker APEX diffractometer (Mo- K_a radiation, $\lambda = 0.71073$ Å).

2-(2'-Hydroxyphenyl)-2-thiazoline (Hthoz): 2-(2'-Hydroxyphenyl)-2-thiazoline was prepared according to the reported procedure with some modification.^[6] The pure ligand was obtained by recrystallization from methanol without the need for flash chromatography. M.p. 45 °C. C₉H₉NOS: calcd. C, 60.31; H, 5.06; N, 7.81%. Found: C, 60.23; H, 5.01; N, 7.83%. **IR** (KBr, selected frequency): $\tilde{v} = 1624(s, C=N) \text{ cm}^{-1}$. ¹**H NMR** (500 MHz, CDCl₃): $\delta = 3.39$ (t, 2 H), 4.51 (t, 2 H), 6.90 (t, 1 H), 7.03 (d, 1 H), 7.38 (m, 1 H), 7.45 (m, 1 H), 12.7 (s, 1 H). ¹³**C NMR** (500 MHz, CDCl₃): $\delta = 32.3$, 63.8, 116.6, 117.4, 119.2, 131.3, 133.7, 158.3, 172.8.

Synthesis of the Complex [Fe(thoz)₂Cl]: To a solution of FeCl₃·6H₂O (0.270 g, 1.00 mmol) in ethanol (15 mL) was added a solution of the ligand, 2-(2'-hydroxyphenyl)-2-thiazoline, (0.358 g, 2.00 mmol) in ethanol (10 mL). After 2 h stirring at room temperature, the solution was filtered and evaporated under reduced pressure to give the complex. Recrystallization from ethanol yielded the complex as dark brown crystals. Yield: 0.337 g, 73%. C₁₈H₁₆ClFeN₂O₂S₂: calcd. C 48.2; H 3.58; N 6.25%; found: C 47.9; H 3.53; N 6.31%. **IR** (KBr, selected frequency): $\tilde{v} = 1611$ (C=N) cm⁻¹.

General Procedure for Sulfide Oxidation: To a solution of sulfide (0.2 mmol), chlorobenzene (0.2 mmol) as internal standard and [Fe(thoz)₂Cl] (0.01 mmol) in a 1:1 mixture of CH₃OH/CH₂Cl₂ (1 mL) was added UHP (0.4 mmol) as a oxidant. The mixture was stirred at room temperature and the reaction progress was monitored by GC. Assignments of products were made by comparison with authentic samples.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-946247 for [Fe(thoz)₂Cl] (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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