Retracted: A new nano bismuth(III) salophen catalyst for green and efficient catalytic oxidation of sulfides into the corresponding sulfoxides

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Retraction
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Abstract
Bismuth(III) salophen as a new catalyst has been synthesized. Structural properties of this complex have been studied by Fourier transform infrared spectroscopy, X-ray diffraction, differential scanning calorimetry, and thermal gravimetric analyses. The average crystalline size of Bi-salophen particles was 86 nm. Thermal analyses show that the complex is stable over 300°C. Catalytic activity of this catalyst has been investigated in oxidation of sulfides. Different kinds of sulfides have been oxidized to the corresponding sulfoxides efficiently in the presence of sodium periodate as oxidant in glacial acetic acid as solvent at room temperature. These sulfides were selectively and completely converted into their corresponding sulfoxides in very short reaction times. Selectivity of this method was excellent, which is another advantage of this method.

Keywords: Bismuth(III) Schiff base, Oxidation, Sodium periodate, Sulfides, Salophen

Background
Schiff base complexes have been extensively used in a variety of applications including biological [1], clinical [2], analytical [3], and catalysis [4-11]. Recently, a number of reports have appeared describing the use of a Schiff base complex as a catalyst in the oxidation of sulfides [12-14]. On the other hand, many recent papers are describing the use of ecologically friendly bismuth compounds in organic transformations [15]. In addition, bismuth derivatives have been widely used in medicine [16]. They have attracted much attention because they are easy to handle, low in cost, and relatively insensitive to air and moisture [17]. In combining these two areas of interest, we are encouraged to use a Bi-salophen complex in the selective oxidation of sulfides into the corresponding sulfoxides (Scheme 1) which is an important method in organic synthesis because sulfoxides are useful synthetic intermediates for the construction of various chemically and biologically significant molecules [18]. Although there are several reagents available for this key transformation [19-27], finding more efficient and selective reagents is of a great challenge in organic transformations. Despite the need for careful control of the reaction temperature, reaction time and relative amounts of oxidants, it is difficult to avoid completely such over-oxidation [28-30]. As the sulfoxides are important for C-C bond formation and functional group transformations, and in view of the recent trend on the catalytic processes towards the development of clean and green chemical processes, the search for newer methods for the catalytic selective oxidation of sulfides to the corresponding sulfoxides has continued.

Methods
Materials and apparatus
Bismuth(III) nitrate pentahydrate was purchased from Fluka (acquired by Sigma-Aldrich Corporation, St. Louis, MO, USA) and used as received. Glacial acetic acid was purchased from Merck AG (Darmstadt, Germany). All
other chemical compounds were commercially available from Merck or Fluka.

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a Bomem MB 104 spectrometer (ABB Ltd., Zurich, Switzerland) using KBr pellets in the 400- to 4,000-cm$^{-1}$ range. Powder X-ray diffraction (XRD) measurements were performed using a BRUKER D8 Advance diffractometer (Ettlingen, Germany). Scans were taken with a 2$\theta$ step size of 0.02 and a counting time of 1.0 s using Cu-K$\alpha$ radiation source generated at 40 kV and 30 mA. Specimens for XRD were prepared by compaction into a glass-backed aluminum sample holder. Data were collected over a 2$\theta$ range from 4° to 70°, and phases were identified by matching experimental patterns to entries in the Diffracplus version 6.0 indexing software (BRUKER AXS, Ettlingen, Germany). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using the simultaneous thermal analyzer apparatus of Rheometric Scientific Company (STA 1500+ Model, England) under a flow of dry air. The temperature was raised from room temperature to 600°C using a linear programmer at a heating rate of 5°C/min.

**General procedure for synthesis of Bi-salophen**

In a 100-mL three-necked round-bottomed flask, Bi(NO$_3$)$_3$·5H$_2$O (1.455 g, 3 mmol), ethanolic solution (25 mL) of o-phenylenediamine (0.324 g, 3 mmol), and salicylaldehyde (0.732 g, 6 mmol) were added. The resulting mixture was stirred and refluxed for 4 h on an oil bath. The progress of the reaction was monitored by thin layer chromatography (TLC) (eluent: n-hexane/ethyl acetate, 1/8) until the initial phenylenediamine spot disappeared. The creamy precipitate was filtered off, washed with cold ethanol and toluene, and then was dried in the air. Melting point (mp) = 302°C (decomposed). Analytically calculated for C$_{20}$H$_{14}$N$_3$O$_5$·5H$_2$O were Bi, 32.69%; C, 37.57%; H, 3.15%; and N, 6.57%, and found values were Bi, 32.83%; C, 37.72%; H, 3.24%; and N, 6.81. FT-IR (KBr pellets, cm$^{-1}$) were 1,612, 1,379, 756, 814, and 3,452 cm$^{-1}$.

**General procedure for oxidation of sulfide**

In a 25-mL flask equipped with a magnetic stirring bar, a solution of sodium periodate (0.0639 g, 0.3 mmol in 1 mL H$_2$O) was added to a mixture of sulfide (0.1 mmol) and Bi-salophen (0.00293 g, 0.005 mmol) in glacial acetic acid (1 mL). The progress of the reaction was monitored by TLC (eluent: n-hexane-ethyl acetate, 7/2). After the reaction was completed, the product was extracted with CH$_2$Cl$_2$ (20 mL) and purified by a silica gel plate or a silica gel column. The identification of the product was confirmed by mp, FT-IR and $^1$H-NMR spectral data.

**Results and discussion**

**Catalyst characterization**

**FT-IR spectroscopy**

The FT-IR spectrum of the complex is in agreement with the proposed structure shown in Figure 1. A wide and strong band at 1,379 cm$^{-1}$ strongly indicates that the nitrate ion is a counter ion. The characteristic bands corresponding to starting aldehyde and amine also disappeared. The other informative band is at 1,612 cm$^{-1}$ due to the stretching frequency of C = N which shows a shift toward a lower frequency due to coordination of nitrogen. The O-H stretching frequency in the free ligand also disappeared which indicates that both oxygen lost their protons and coordinated with the bismuth ion.

**X-Ray diffraction**

In addition to common characterization tools, XRD was also used for the identification of crystalline phases and the evaluation of crystallite sizes using the Scherrer equation [20]. The average of crystalline size of Bi-salophen particles was 86 nm which was calculated from the most intense Bi-salophen line (2$\theta$ = 13°) in the XRD spectrum (Figure 2). The spectrum indicates the presence of cubic and tetragonal forms of the catalyst.
Thermal gravimetric analysis and differential scanning calorimetry

Thermal analyses were also performed to measure the stability of the catalyst as well as the amount of water of crystallization. The TGA/DSC curves for this catalyst are shown in Figure 3. The weight losses agreed fairly well with those expected for the decomposition of this complex. For this catalyst, the thermogravimetric curve seems to indicate a three-stage decomposition. The first endothermic stage is considered to be due to the removal of all three water of crystallization (70°C to 90°C), and the second endothermic stage (95°C to 295°C) is due to the decomposition of salophen and/or breaking of Bi-O bonds, respectively. The latter temperature is equal to the decomposition point measured individually by the melting point apparatus. The third endothermic peak which was around 305°C to 370°C is due to the decomposition of bismuth nitrate to the corresponding oxide. The TGA curve is involved with a total overall weight loss of ca. 66 wt.%.

Investigation of Bi-salophen catalytic activity

In a preliminary approach to the periodate anion activation by metal Schiff base complexes, we decided to investigate the activity of Bi-salophen in the catalytic oxidation of sulfides with NaIO₄. The results are summarized in Table 1. A series of diaryl, dialkyl, dibenzyl, diallyl, aryl benzyl, alkyl aryl, cyclic, and heterocyclic sulfides underwent selective oxidation to afford the corresponding sulfoxides at room temperature and at short reaction times. Alkyl aryl sulfides were selectively and completely converted into their corresponding sulfoxides in very short reaction times (Table 1, entries 1 to 3). In comparison, some transition metal Schiff base complexes were used for the catalytic oxidation of methyl phenyl sulfide but in very long reaction times (Table 2, entries 1 to 5). In addition, some of these systems suffer from other disadvantages such as production of sulfone as a side product due to over-oxidation [12]. Therefore, it is concluded that our system shows great advantages such as mild reaction conditions, shorter reaction times, selective and controlled oxidation, and a nontoxic catalyst employment.

Diphenyl sulfide was converted into diphenyl sulfoxide in an excellent yield (Table 1, entry 4). In comparison, the formation of sulfoxides from diaryl sulfides has been reported in very long reaction times and relatively hard reaction conditions, and sulfone has been produced as a side product due to over-oxidation [35-37].

Another useful feature of the presented protocol can be seen in the cases of benzyl aryl and dibenzyl sulfides (Table 1, entries 5 to 7), and diallyl sulfide (Table 1,
entry 12). No oxidation was observed at the benzylic C-H bonds in the former cases. Also, neither over-oxidation to sulfone nor epoxidation of the double bond was observed in the latter case. Dibenzothiophene was selectively and completely converted into the corresponding sulfoxide in very short reaction times (Table 1, entry 8). In comparison, some transition metal Schiff base complexes were used for the catalytic oxidation of dibenzothiophene, but sulfone was produced as a side product due to over-oxidation [37].

**Conclusions**

In the course of our research, we found that bismuth(III) salophen is relatively nontoxic, easily synthesized on any scale at low cost, and fairly stable to water, unlike common Lewis acids (e.g., AlCl₃) which readily decompose in aqueous media and selectively catalyze the oxidation of sulfides into their corresponding sulfoxides in very short reaction times and excellent yields.

**Competing interests**

The authors declare that they have no competing interest.

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**Authors’ contributions**

MGT participated in the experiments, MJ carried out the experiment, ER participated in the interpretation of organic transformations. MF participated in preparation and study of spectra. MJ conceived the study and participated in its design and coordination. All authors read and approved the final manuscript.

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### Table 1 Oxidation of sulfides with NaIO₄ catalyzed by Bi-salophen

| Entry | Sulfides | Sulfoxides (%) | Time (min) |
|-------|----------|----------------|------------|
| 1     | ![Image](image1.png) | 100 | 6 |
| 2     | ![Image](image2.png) | 100 | 6 |
| 3     | ![Image](image3.png) | 95 | 7 |
| 4     | ![Image](image4.png) | 94 | 6 |
| 5     | ![Image](image5.png) | 94 | 5 |
| 6     | ![Image](image6.png) | 92 | 5 |
| 7     | ![Image](image7.png) | 95 | 8 |
| 8     | ![Image](image8.png) | 98 | 8 |
| 9     | ![Image](image9.png) | 100 | 5 |
| 10    | ![Image](image10.png) | 100 | 5 |
| 11    | ![Image](image11.png) | 98 | 5 |
| 12    | ![Image](image12.png) | 96 | 5 |

Reaction condition: sulfide (0.1 mmol), NaIO₄ (0.3 mmol), Bi–salophen (0.005 mmol) in glacial acetic acid/H₂O (1:1) at room temperature.

### Table 2 Comparative oxidation of methyl phenyl sulfide by some metal Schiff base systems

| Entry | Metal | Oxidant | Time (h) | Yield (%) | Reference |
|-------|-------|---------|----------|-----------|-----------|
| 1     | Mn    | PhIO    | 5        | 70        | [12]      |
| 2     | Ti    | H₂O₂    | 24       | 82        | [31]      |
| 3     | Fe    | PhIO    | 2        | 88        | [32]      |
| 4     | V     | H₂O₂    | 12       | 81        | [33]      |
| 5     | Cu    | H₂O₂    | 4.5      | 90        | [34]      |
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