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Synthesis and characterization of insoluble cobalt(II), nickel(II), zinc(II) and palladium(II) Schiff base complexes: Heterogeneous catalysts for oxidation of sulfides with hydrogen peroxide



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ABSTRACT

The condensation reaction of 1,2-bis(2'-aminophenoxy)benzene with 2-pyridinecarbaldehyde in a mole ratio of 1:2 gives a new Schiff base ligand (**L**). Four Schiff base complexes, **CoL(NO₃)₂** (**1**), **NiLCl₂** (**2**), **ZnL(NO₃)₂** (**3**) and **Pd₂LCl₄** (**4**) have been prepared by direct reaction of the ligand (**L**) and appropriate metal salts. The Schiff base ligand (**L**) has been characterized by IR, ¹H NMR and ¹³C NMR spectroscopy and elemental analysis. Also, all complexes have been characterized by IR and XRD spectroscopy techniques and elemental analysis. The synthesized complexes have very poor solubility in all polar and non-polar solvents such as: H₂O, MeOH, EtOH, CH₃CN, DMSO, DMF, CHCl₃, CH₂Cl₂, THF, etc; therefore, they have been used as heterogeneous catalysts. Catalytic performance of the complexes was studied in oxidation of thioanisole using hydrogen peroxide (H₂O₂) as the oxidant. Various factors including the reaction temperature, amount of oxidant and catalyst amount were optimized. The palladium Schiff base complex, **Pd₂LCl₄** (**4**), shows better catalytic activity than other complexes. Therefore, the Pd(II) Schiff base complex has been used as a catalyst for oxidation of different sulfides to their corresponding sulfones in acetonitrile with hydrogen peroxide as the oxidant. The palladium Schiff base complex, **Pd₂LCl₄** (**4**), has shown a very good recyclability, up to five times, without any appreciable decreases in catalytic activity and selectivity.

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1. Introduction

Oxidation of sulfides is the most straightforward method for the synthesis of sulfoxides and sulfones [1]. Sulfoxides and sulfones are important intermediates for

pharmaceuticals, polymer materials and ligands in asymmetric catalysis. Also, these compounds could be used as oxotransfer reagents and biologically active molecules [1,2].

Many kinds of oxidants such as nitric acid, organic peroxides, and heavy metal oxidants have been employed as effective oxidants to form sulfoxides and/or sulfones in high yields [1]. Among various kinds of oxidants, hydrogen peroxide (H₂O₂) is one of the most straightforward, clean, and versatile oxidants from both an environmental and

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economic perspective because H_2O_2 has a high content of active oxygen and its byproduct is water [3]. It is well known that sulfides are oxidized to generate sulfoxides and sulfones by H_2O_2 at an elevated temperature and/or with a long reaction time without a metal catalyst [4]. However, highly selective oxidation of sulfides under mild reaction conditions is achieved by the application of optimized catalysts and/or reaction systems [5].

Schiff bases have played an important role in the development of coordination chemistry; for example, they readily form stable complexes with most of the transition metals. Also, these compounds are often used as catalysts for oxidation reactions under different conditions [6–10]. Although Schiff base complexes are often used as efficient homogeneous catalysts for the oxidation reaction, some problems often exist in these types of oxidation studies such as (1) deactivation, (2) instability and (3) expensive recycling of these homogeneous systems [11]. So, for improving the performance of catalytic activity, scientists tried to convert them into heterogeneous ones in some different ways. The greatest advantage of heterogeneous catalysis is the facile separation of catalysts from the reaction media and products [12]. In order to fix catalysts into heterogeneous supports, different ways can be used, classified as: (1) immobilization in zeolites, (2) grafting onto inorganic supports such as silica, and (3) copolymerization and attachment of the catalyst onto an organic polymer and use of insoluble complexes as heterogeneous catalysts without any supports [12,13]. The latter is a very good way for synthesis of heterogeneous catalysts because of removal of some synthesis steps. However, a major challenge is design of insoluble catalysts with high yields, selectivity, and cost effectiveness. According to all the above discussion, insoluble Schiff base complexes with good stability and catalytic activity are still rare and lack generality. Most of the Schiff base complexes that are used as heterogeneous catalysts form covalent bonds or electrostatic interactions with organic polymers.

This paper is a continuation of our previous study on Schiff base ligands and complexes with *ortho*-aminophenyl diamines [14]. In our previous study, we reported the crystal and molecular structure of the precursory 1,2-bis(2'-nitrophenoxy)-4-methylbenzene prepared from an achiral molecule (4-methylcatechol), in which the two phenoxy groups are placed to one another in such a way that the molecule is C_1 symmetrical, i.e., chiral. The chiral conformation of 1,2-bis(2'-nitrophenoxy)-4-methylbenzene after reduction is maintained in complexation with zinc(II) and cobalt(II). This implies that in Schiff base ligands derived from *ortho*-aminophenyl diamines, the two α -diimine systems form an octahedral cavity having the same chirality as that of the precursory diamine [14]. In a continuation of this study, herein we report the synthesis and characterization of four new Schiff base complexes, **CoL(NO₃)₂** (**1**), **NiLCl₂** (**2**), **ZnL(NO₃)₂** (**3**) and **Pd₂LCl₄** (**4**) derived from 1,2-bis(2'-aminophenoxy)benzene and 2-pyridinecarbaldehyde. These complexes have very poor solubility in all polar and non-polar solvents. This parameter (insolubility) causes these complexes to be suitable for acting as heterogeneous catalysts without attachment to

organic/inorganic supports. Therefore, these complexes have been used for selective heterogeneous oxidation of sulfides in acetonitrile. The results showed high stability and reusability in oxidation reactions.

2. Experimental

2.1. Physical methods

Infrared spectra (KBr pellets) were recorded on a JASCO, FT/IR-6300 instrument. The elemental analysis (CHN analysis) was carried out on Leco, CHNS-932 and PerkinElmer 7300 DV elemental analyzers. Powder X-ray diffraction (XRD) data were obtained on a D8 Advanced Bruker using $\text{Cu K}\alpha$ radiation ($2\theta = 5\text{--}70^\circ$). The oxidation products were quantitatively analyzed by gas chromatography (GC) on a Shimadzu GC-16A instrument using a 2 m column packed with a silicon DC-200 and an FID detector. ^1H and ^{13}C NMR spectra of the ligand were recorded on a Bruker Avance 400 spectrometer using CDCl_3 as the solvent.

2.2. Reagents

All chemicals used were of analytical grade and were used as received without any further purification and were obtained from Sigma–Aldrich. 1,2-bis(2'-aminophenoxy)benzene was prepared according to literature methods [15].

2.2.1. Synthesis of the Schiff base ligand (L)

2-Pyridinecarboxaldehyde (4 mmol) in absolute EtOH (50 mL) was added dropwise to a boiling solution of 1,2-bis(2'-aminophenoxy)benzene (2 mmol) in absolute EtOH (25 mL). The solution was gently refluxed for 12 h. Then, the solvent volume was reduced by using a rotary evaporator (~5 mL) and cooled in an ice bath for 5 h. The precipitate was filtered off and washed with cold EtOH and dried *in vacuo*. Yield: 58%. Anal. Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_4\text{O}_2$, C, 76.4; H, 4.7; N, 11.8. Found: C, 76.5; H, 4.8; N, 11.8%. ^1H NMR δ_{H} (300 MHz, CDCl_3): 9.29 (2H, HC=N), 8.87 (2H, pyridine), 8.16 (2H, pyridine), and 8.01–6.63 (aromatic (12H) and pyridine (4H)) ppm. ^{13}C NMR δ_{C} (300 MHz, CDCl_3): 163.51 (C=N)_{imi}, and 150.34–115.34 (aromatic and pyridine rings) ppm. IR: 1637 (CH=N)_{imi}, 1601 (CH=N)_{py}, and 1488 (C=C)_{py}.

2.2.2. Preparation of complexes

2.2.2.1. General synthesis. 2-Pyridinecarboxaldehyde (4 mmol) in dry ethanol (50 mL) was added dropwise to a boiling solution of 1,2-bis(2'-aminophenoxy)benzene (2 mmol) in the same solvent (25 mL). The solution was stirred and refluxed for 12 h and then the appropriate salt (2 mmol) in EtOH (20 mL) was added dropwise. Upon addition, immediate precipitation of complexes occurs. The solution was refluxed for 6 h, and concentrated in a rotary evaporator until approximately 10–15 mL. The obtained precipitate was filtered, subsequently washed with EtOH and then dried in air.

2.2.2.2. Ni complex NiLCl₂. Yield: (87%). Anal. Calcd for $\text{C}_{30}\text{H}_{22}\text{Cl}_2\text{N}_4\text{NiO}_2$: C, 60.04; H, 3.70; N, 9.34. Found: C,

60.09; H, 3.74; N, 9.39%. IR: 1635 (CH=N)_{imi}, 1595 (CH=N)_{py}, and 1483 (C=C)_{py}, 404 (M – N).

2.2.2.3. *Co complex CoL(NO₃)₂*. Yield: (81%). Anal. Calcd for C₃₀H₂₂CoN₆O₈: C, 55.14; H, 3.39; N, 12.86. Found: C, 55.06; H, 3.43; N, 12.79%. IR: 1628 (CH=N)_{imi}, 1595 (CH=N)_{py}, 1485 (C=C)_{py}, 1456 and 1318 (NO₃), 403 (M – N).

2.2.2.4. *Zn complex ZnL(NO₃)₂*. Yield: (94%). Anal. Calcd for C₃₀H₂₂N₆O₈Zn: C, 54.60; H, 3.36; N, 12.73. Found: C, 54.65; H, 3.41; N, 12.69%. IR: 1633 (CH=N)_{imi}, 1595 (CH=N)_{py}, 1485 (C=C)_{py}, 1456 and 1323 (NO₃), 407 (M – N).

2.2.2.5. *Pd complex Pd₂LCl₄*. Yield: (92%). Anal. Calcd for C₃₀H₂₂Cl₄N₄O₂Pd₂: C, 43.67; H, 2.69; N, 6.79. Found: C, 43.69; H, 2.68; N, 6.83%. IR: 1619 (CH=N)_{imi}, 1587 (CH=N)_{py}, and 1488 (C=C)_{py}, 412 (M – N).

2.3. Catalytic activity and optimization of reaction conditions

After the synthesis of **CoL(NO₃)₂** (**1**), **NiLCl₂** (**2**), **ZnL(NO₃)₂** (**3**) and **Pd₂LCl₄** (**4**) Schiff base complexes, we decided to investigate the catalytic activity of the complexes in oxidation of sulfides with H₂O₂ as the oxidant under different reaction conditions.

2.3.1. Oxidation of thioanisole with H₂O₂ catalyzed by Co, Ni, Zn and Pd Schiff base complexes

To find the optimized conditions, we investigated the oxidation of thioanisole as a model substrate using hydrogen peroxide (Scheme 1). Generally, oxidation of thioanisole gives a sulfoxide and sulfone. In our catalytic reaction sulfone is formed as the major product (Scheme 1). The effect of different reaction parameters (H₂O₂ amount, temperature and amount of catalyst) was studied on the thioanisole oxidation.

2.3.2. General procedure for catalytic oxidation of sulfides in acetonitrile

A mixture of 1 mmol sulfide and H₂O₂ (3 mmol) was added to a stirring solution of **CoL(NO₃)₂** (**1**), **NiLCl₂** (**2**), **ZnL(NO₃)₂** (**3**) and **Pd₂LCl₄** (**4**) Schiff base complexes (0.01 mmol) in acetonitrile (3 ml) at 50 °C for the required period of time (4 h). After completion of the reaction (TLC), the catalyst was separated by filtration, washed three times with acetonitrile and then dried under vacuum and used for the next oxidation cycle. The products were analyzed by GC using diphenyl sulfide as the internal standard. NMR

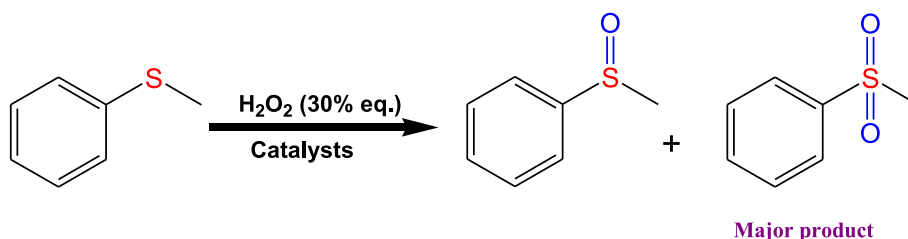
spectra of the products (sulfone) are available in [Supplementary data](#).

3. Results and discussion

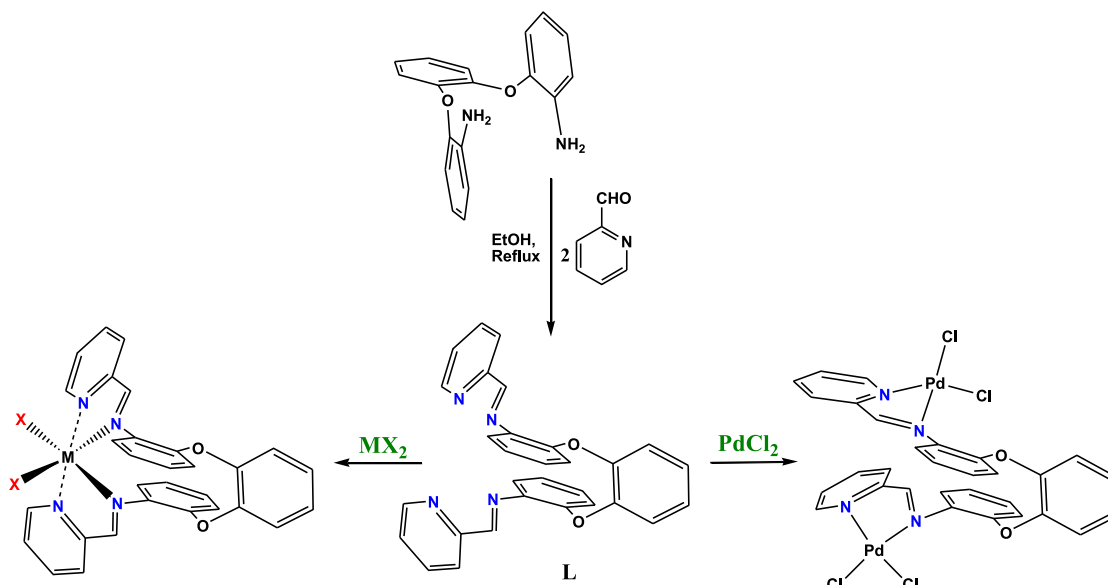
3.1. Characterization of Schiff base ligand and complexes

The procedure for the synthesis of the Schiff base ligand, **L**, is reported in [Scheme 2](#). The ligand was obtained by the self-condensation reaction between 1,2-bis(2'-amino-phenoxy)benzene and 2-pyridinecarboxaldehyde with ethanol as the solvent under reflux conditions. The chemical structure of the ligand was confirmed by elemental analysis and IR, ¹H NMR and ¹³C NMR spectroscopy. Formation of the Schiff base ligand is evidenced by the presence of a strong IR band at 1637 cm⁻¹ due to ν(C=N), while no bands attributable to ν(C=O) or ν(NH₂) have been detected. The bands at 1601 and 1488 cm⁻¹ of the pyridine ring vibrations are also present in the IR spectrum of the ligand [16]. The ¹H NMR spectrum is consistent with the IR observations. The ¹H NMR spectrum in CDCl₃ shows a peak at 9.29 ppm corresponding to the imine protons of the ligand. Cobalt(II), Nickel(II), Zinc(II) and Palladium(II) Schiff base complexes, **CoL(NO₃)₂** (**1**), **NiLCl₂** (**2**), **ZnL(NO₃)₂** (**3**) and **Pd₂LCl₄** (**4**), were synthesized by the reaction of Co(NO₃)₂·6H₂O, NiCl₂·6H₂O, Zn(NO₃)₂·6H₂O and PdCl₂ with the tetradentate Schiff base ligand, **L**, in ethanol under reflux conditions, respectively (Scheme 2). All of the Schiff base complexes are stable in air. Their photographic images are shown in [Fig. 1](#). The bands in the range of 1619–1635 cm⁻¹ were assigned to the –CH=N– group. The imine peak of the complexes showed a red-shift of ca. 2–18 cm⁻¹ compared to that of the ligand, indicating the coordination of the imine nitrogen to the metal ions (Scheme 2) [17,18]. This feature can be explained by the withdrawal of electrons from the nitrogen atom to the metal ion due to the coordination process. The IR spectra exhibit medium to strong bands at ~1595 and ~1480 cm⁻¹ as expected for the two highest energy pyridine-ring vibrations. The shift of the imine and pyridine bands by complexation suggests coordination *via* the imine and pyridine nitrogen atoms. Another conclusive evidence for the formation of the M–N bond is also shown by the appearance of a new band at around 405 cm⁻¹ which could be assigned to the M–N stretching vibrations [19].

When the fundamental IR bands of the NO₃⁻ group would be identified, it is possible to tell if the NO₃⁻ group is ionic or coordinated. The occurrence of two strong



Scheme 1. Oxidation of thioanisole with hydrogen peroxide in the presence of **CoL(NO₃)₂** (**1**), **NiLCl₂** (**2**), **ZnL(NO₃)₂** (**3**) and **Pd₂LCl₄** (**4**) Schiff base complexes as catalysts.



MX_2 : $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

Scheme 2. Synthetic routes for the preparation of Schiff base complexes.

absorption bands in the complexes under study, **1** and **2**, at ~ 1450 and $\sim 1320 \text{ cm}^{-1}$ is attributed to ν_4 and ν_1 modes of vibrations of the covalently bonded nitrate groups, respectively. This suggests that nitrate groups are present inside the coordination sphere [20,21]. Also, if the $(\nu_4 - \nu_1)$ difference is taken as an approximate measure of the covalency of the nitrate group [22,23], a value of $\sim 200 \text{ cm}^{-1}$ for the complexes studied suggests strong covalency of the metal-nitrate bonding. The strong and sharp band at $\sim 1384 \text{ cm}^{-1}$ is characteristic of ionic nitrate. As depicted in Fig. 2, we do not observe this peak in the IR spectrum of zinc(II) and cobalt(II) complexes.

Devi *et al.* have shown that the number and relative energies of nitrate combination frequencies ($\nu_1 + \nu_4$) in the $1700\text{--}1800 \text{ cm}^{-1}$ region of the infrared spectrum may be used as an aid to distinguish the various coordination modes of the nitrate groups [24]. According to Agarwal

et al. bidentate coordination involves a greater distortion from D_{3h} symmetry than monodentate coordination; therefore, bidentate complexes should show a larger separation of $(\nu_1 + \nu_4)$ [25]. By studying the spectra of a number of compounds with known crystal structures, Devi *et al.* [24] showed that the separation of monodentate nitrate groups appeared to be $5\text{--}26 \text{ cm}^{-1}$ and that of bidentate groups to be $25\text{--}66 \text{ cm}^{-1}$. However, these absorptions are very weak and can only be used for diagnosis when there are no other absorptions in this region. The authors have tried to apply this method for cobalt (II) and zinc(II) complexes. In both cases, $\text{CoL}(\text{NO}_3)_2$ (**1**) and $\text{ZnL}(\text{NO}_3)_2$ (**3**), a separation of $20\text{--}25 \text{ cm}^{-1}$ in the combination bands ($\nu_1 + \nu_4$) in the $1700\text{--}1800 \text{ cm}^{-1}$ region concludes the monodentate nitrate coordination. On the basis of the above discussion, a six-coordinated structure is



Fig. 1. The photographic images of $\text{CoL}(\text{NO}_3)_2$ (**1**), $\text{ZnL}(\text{NO}_3)_2$ (**3**) and Pd_2LCl_4 (**4**) Schiff base complexes from left to right. The color of $\text{NiL}(\text{NO}_3)_2$ (**2**) and $\text{ZnL}(\text{NO}_3)_2$ (**3**) Schiff base complexes are identical.

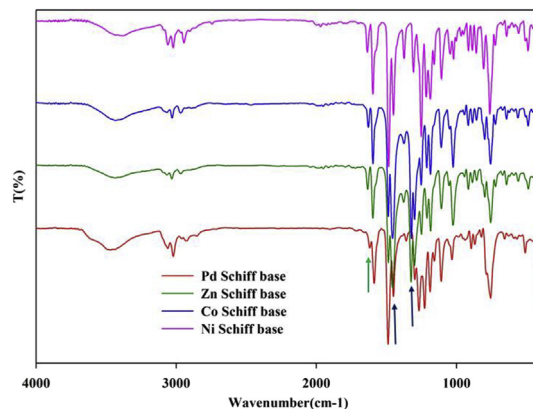


Fig. 2. FT-IR spectra of $\text{CoL}(\text{NO}_3)_2$ (**1**), $\text{NiL}(\text{NO}_3)_2$ (**2**), $\text{ZnL}(\text{NO}_3)_2$ (**3**) and Pd_2LCl_4 (**4**) Schiff base complexes. Important peaks are indicated by arrows (see the text).

proposed for cobalt (II), zinc(II) and nickel(II) complexes in which the metal ions coordinate *via* four azomethine nitrogens and the two remaining coordination sites are occupied by two oxygen atoms of two monodentate NO_3^- groups in zinc and cobalt complexes and by two Cl atoms in the nickel complex (Scheme 2). As we know, six-coordinate structures are very common for Co(II), Ni(II) and Zn(II) complexes. It should be noted that these structures were confirmed in our previous work by X-ray crystallography [14].

Because of the great size of the palladium atom and impossibility of the octahedral structure for palladium complex, we suggest different coordination modes for the Pd(II) complex. This proposed structure was confirmed by elemental analysis. It should be noted that in our previous work, we proved that the four azomethine nitrogen atoms of the ligand are not able to provide a square planar conformation when the metal atom lies in the ligand cavity [14]. For this reason, the metal atom must be out of the ligand cavity if a square planar configuration is assumed for the metal ion (Scheme 2). As shown in Scheme 2, we suggest a bimetallic structure for the Pd(II) complex. Each Pd(II) atom is coordinated to one pyridine nitrogen and one azomethine nitrogen. Two remaining coordination sites are occupied by two Cl atoms.

Fig. 3 shows the X-ray powder diffraction pattern of four Schiff base complexes. As depicted in Fig. 3, the XRD patterns of $\text{CoL}(\text{NO}_3)_2$ (1), NiLCl_2 (2) and $\text{ZnL}(\text{NO}_3)_2$ (3) are almost identical.

3.2. Application of Schiff base complexes for the oxidation of sulfides

In order to optimize the reaction conditions, we surveyed the oxidation reaction of thioanisole as a model compound using 30% H_2O_2 under various reaction conditions in terms of time and product yield.

3.2.1. Effect of H_2O_2 amounts on the oxidation of thioanisole

In order to determine the role of H_2O_2 amounts on the oxidation of thioanisole to the corresponding sulfone and sulfoxide, the mole ratio of H_2O_2 /thioanisole was changed,

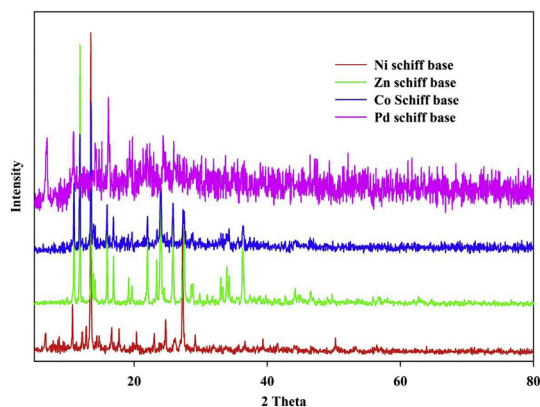


Fig. 3. XRD pattern of $\text{CoL}(\text{NO}_3)_2$ (1), NiLCl_2 (2), $\text{ZnL}(\text{NO}_3)_2$ (3) and Pd_2LCl_4 (4) Schiff base complexes.

keeping all other parameters fixed: catalysts (5 mg), temperature (50 °C) and reaction time (4 h). The results are shown in Table 1.

For all four complexes, H_2O_2 /thioanisole molar ratios from 1:1 to 4:1 resulted in 9%–72% conversion. When this molar ratio was changed to 1:4, conversion increased but sulfoxide selectivity decreased for four complexes. However, the conversion was found to decrease for thioanisole/ H_2O_2 molar ratios of 1:1 and 1:2. Therefore, a 1:3 molar ratio of thioanisole/ H_2O_2 was found to be the optimum.

3.2.2. Effect of catalyst amounts

The amount of catalyst had a considerable effect on the conversion of thioanisole to the corresponding sulfone. The results are given in Table 2. Four various amounts, 1, 5, 10 and 20 mg, were used for all the catalysts and thioanisole (1 mmol), H_2O_2 (3 mmol), temperature (50 °C) and the reaction time (4 h) were fixed. For all complexes the lower conversion of thioanisole into the corresponding sulfone with 1 mg of catalysts may be as a result of fewer catalytic sites. The maximum conversion was observed with 5 mg of catalysts for all four complexes, but there was no considerable difference in the conversion when 10 and 20 mg of catalysts were employed. Therefore, 5 mg of catalysts were taken as the optimum amount.

3.2.3. Effect of temperature on the reaction

In the present work for optimization of the reaction conditions, we also studied the effect of temperature on the catalytic performance of $\text{CoL}(\text{NO}_3)_2$ (1), NiLCl_2 (2), $\text{ZnL}(\text{NO}_3)_2$ (3) and Pd_2LCl_4 (4) complexes (Table 3). The effect of temperature on the catalytic activity of the four catalysts was studied at four different temperatures, 25 °C, 50 °C, 60 °C and reflux (85 °C) with a constant amount of thioanisole (1 mmol), H_2O_2 (3 mmol) and catalyst (5 mg) in 3 mL of acetonitrile (Table 3). The maximum conversion, 77%, with 99% selectivity for sulfones was obtained when the reaction was carried out at 85 °C for the Pd complex. At

Table 1

Oxidation of thioanisole with various amounts of H_2O_2 in the presence of Co, Ni, Zn and Pd Schiff base complexes.^a

Entry	Catalyst	mmol H_2O_2	Conversion (%) ^b	Selectivity (%) ^c
1	Co	1	9	60
2	Co	2	14	67
3	Co	3	19	71
4	Co	4	23	80
5	Ni	1	24	54
6	Ni	2	31	66
7	Ni	3	36	70
8	Ni	4	41	75
9	Zn	1	27	57
10	Zn	2	34	64
11	Zn	3	39	69
12	Zn	4	41	73
13	Pd	1	51	80
14	Pd	2	57	92
15	Pd	3	70	99
16	Pd	4	72	99

^a Reaction conditions: thioanisole (1 mmol), catalyst (5 mg), acetonitrile (3 mL) and H_2O_2 30% at 50 °C for 4 h.

^b Conversion based on sulfide substrates.

^c Selectivity for sulfone.

Table 2
Oxidation of thioanisole with different amounts of catalyst in the presence of H₂O₂.^a

Entry	Catalyst	mg of catalyst	Conversion (%) ^b	Selectivity (%) ^c
1	Co	1	7	45
2	Co	5	19	71
3	Co	10	21	65
4	Co	20	22	63
5	Ni	1	16	51
6	Ni	5	36	70
7	Ni	10	38	64
8	Ni	20	40	61
9	Zn	1	19	53
10	Zn	5	39	69
11	Zn	10	42	66
12	Zn	20	45	63
13	Pd	1	36	79
14	Pd	5	70	99
15	Pd	10	70	80
16	Pd	20	72	81

^a Reaction conditions: thioanisole (1 mmol), acetonitrile (3 mL) and H₂O₂ (3 mmol) at 50 °C for 4 h.

^b Conversion based on sulfide substrates.

^c Selectivity for sulfone.

lower temperatures, the conversion was low but the selectivity for sulfoxide was higher for all complexes. At the reflux temperature, the initial conversion of thioanisole was higher than the conversion at 50 °C, but when the reaction would continue the conversion of thioanisole was almost the same as the conversion at 50 °C. Therefore, 50 °C was selected as the optimum temperature and all the catalytic oxidation reactions were carried out at this temperature. These results showed that the Pd Schiff base complex, **Pd₂LCl₄** (**4**), under optimal reaction conditions exhibits much better catalytic activity compared to the other Schiff base complexes. Therefore, the applicability of the Pd Schiff base complex was studied by oxidation of several types of sulfides with different electronic and steric effects to corresponding sulfones under the optimized conditions (3 mmol H₂O₂, 5 mg catalyst at 50 °C) (Table 4).

Table 3
Oxidation of thioanisole with different catalysts in various temperatures.^a

Entry	Catalyst	Temperature °C	Conversion (%) ^b	Selectivity (%) ^c
1	Co	25	7	25
2	Co	50	19	71
3	Co	60	24	76
4	Co	85	32	91
5	Ni	25	12	31
6	Ni	50	36	70
7	Ni	60	38	76
8	Ni	85	44	88
9	Zn	25	15	30
10	Zn	50	39	69
11	Zn	60	44	73
12	Zn	85	48	89
13	Pd	25	34	53
14	Pd	50	70	99
15	Pd	60	73	99
16	Pd	85	77	99

^a Reaction conditions: thioanisole (1 mmol), acetonitrile (3 mL) and H₂O₂ (3 mmol), 5 mg catalyst for 4 h.

^b Conversion based on sulfide substrates.

^c Selectivity for sulfone.

As shown in Table 4, the sulfides with less and high steric hindrance were converted to the corresponding sulfones in good to excellent yields except DBT (Table 4, entry 9). It is obvious that these types of sulfides are completely not affected under the reaction conditions. Also, the influence of electronic effects was found in the case of 4-nitrophenyl sulfide, which has a negative effect on the reaction time. The chemoselectivity of this catalytic system was also investigated in the selective oxidation of sulfides containing hydroxyl and carbon–carbon double bond groups. These substrates selectively underwent oxidation at the sulfur atom without undergoing further structural changes in their functional group. For example, in the case of allylic sulfides, epoxidation of the double bond was not observed and only the corresponding sulfones were obtained in excellent yields (Table 4, entries 6 and 7). Also, the presence of the hydroxyl group did not interfere with the oxidation process of the sulfide, and the desired sulfone was obtained in excellent yield (Table 4, entry 8). It is clear that these kinds of sulfides are completely unaffected under the reaction conditions, indicating the good ability of this protocol in oxidation of different types of sulfides.

The recycling properties of the Pd Schiff base complex were investigated in methyl phenyl sulfide oxidation at 50 °C using aqueous 30% H₂O₂ for 1 mmol of substrate. After the completion of the first oxidation reaction of thioanisole to the methyl phenyl sulfone under optimized conditions, the catalyst was isolated by filtration, washed with CH₃CN, dried in an oven at 80 °C for 2 h and reused for the next run. Under the described conditions, the catalyst exhibited high catalytic activity up to five times reuse without noticeable decrease in catalytic activity (Fig. 4).

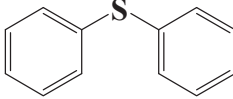
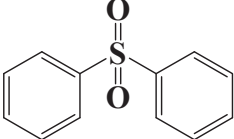
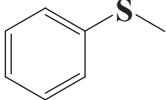
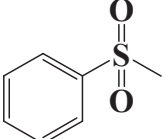

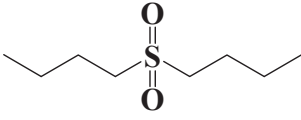
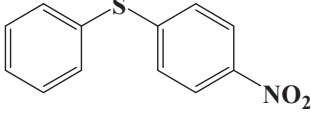
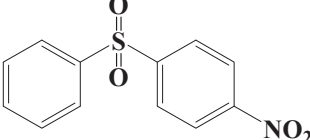

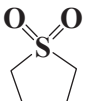
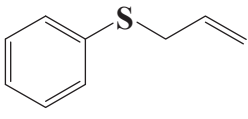
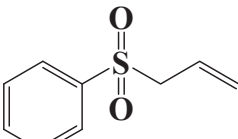
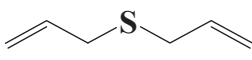
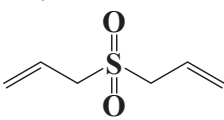
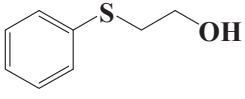
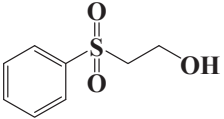
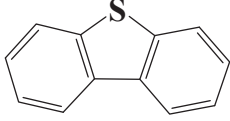
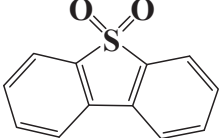
The XRD pattern and FT-IR spectrum of the recovered Pd Schiff base complex indicated that no significant change in the catalyst took place even after reusing five times (Figs. 5 and 6).

3.3. Comparison with other catalysts

Comparative data on the performance of various Schiff base complexes in the oxidation of sulfides are shown in Table 5. As you can see in most of them, the Schiff base complexes can do the selective oxidation of sulfide to sulfoxide. The selective oxidation of sulfides to sulfones with Schiff base complexes as catalysts is very rare.

- Conte *et al.* reported an experimental and theoretical study concerning the effects of steric and electronic modification of the ligands on the catalytic activity of salophen and salen oxo vanadium(V) complexes in the oxidation of PhSMe with H₂O₂. The results indicated that steric factors play a major role in determining the outcome of the reaction (Table 5, entries 1–14) [26].
- Islam *et al.* synthesized a new Co(III) Schiff base complex, (CoL)Cl₂·4H₂O (L = Schiff base), and used this complex as homogeneous (without support) and heterogeneous (with polymer support) catalysts for the oxidation of alkenes and sulfides using H₂O₂ as the oxygen source (Table 5, entries 15–18) [27]. Comparison between catalytic activities of the homogeneous

Table 4The oxidation of various sulfides with Pd Schiff base complex as the catalyst by using 30% aqueous H₂O₂.^a

Entry	Sulfide (Substrate)	Sulfone (Product)	Time (h)	Conversion (%) ^b	Selectivity(%) ^c
1			5.5	72	99
2			4	70	99
3			6	73	99
4			6.5	69	98
5			4.15	74	99
6			6.5	76	99
7			8	75	98
8			4.5	73	99
9			6	21	99

^a Reaction conditions: catalyst (5 mg), substrate (1.0 mmol), H₂O₂ (3 mmol), CH₃CN (solvent, 3 mL), at 50 °C.^b Conversion based on sulfide substrates.^c Selectivity for sulfone.

cobalt complex and the heterogeneous complex was done and it was shown that the polymer anchored cobalt complex is more active than the homogeneous complex. The active sites do not leach out from the polymer support and thus the polymer anchored cobalt catalyst can be reused without appreciable loss of activity, indicating that the anchoring procedure was

effective. The reusability of this catalyst was high and can be reused seven times without significant decrease from its initial activity.

3 Rezaeifard *et al.* investigated oxidation of sulfides using urea hydrogen peroxide (UHP) under the influence of a tridentate Schiff base dioxo-molybdenum(VI) complex catalyst, [MoO₂(L)(CH₃OH)], in ethanol under mild

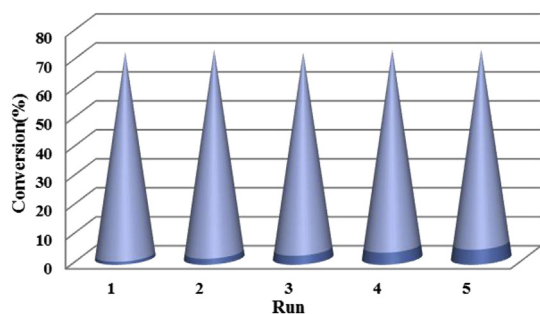


Fig. 4. The recycling experiment of the Pd Schiff base complex in the oxidation reaction of methyl phenyl sulfide to methyl phenyl sulfone under optimized conditions.

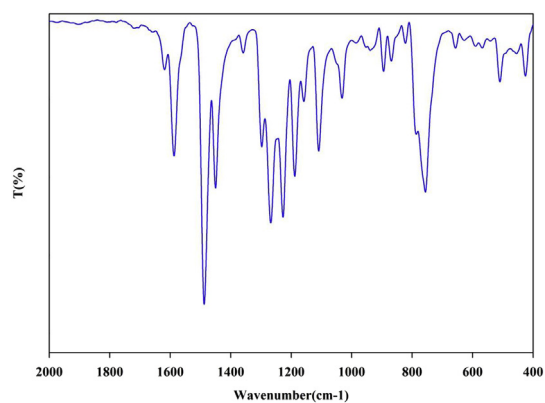


Fig. 6. FT-IR spectrum of the Pd Schiff base complex recovered in run 5.

conditions. Relatively high stability and desired turnover numbers have been observed for this Mo-catalyst in oxidation of sulfides to both sulfoxides and sulfones (Table 5, entries 19–22) [28].

- 4 Barman *et al.* reported selective oxidation of sulfide to sulfoxide with 30% H_2O_2 catalyzed by the copper(II)–Schiff base complex. The reactions proceed under mild conditions in acetonitrile at room temperature to provide a variety of aryl and alkyl sulfoxides in excellent yield (Table 5, entries 23–24) [10].
- 5 Liu *et al.* presented two chiral robust porous MOFs containing μ -oxo-bis[Fe(salen)] dimers and demonstrated their efficient enantioselective abilities to catalyze oxidation of sulfides to sulfoxides with comparable catalytic performance relative to the homogeneous catalysts. These two compounds were efficient and recyclable heterogeneous catalysts for asymmetric oxidation of sulfides to sulfoxides with an enantioselectivity up to 96% (Table 5, entries 25–26) [29].
- 6 In our previous work, we have synthesized a new bidentate NO donor ligand, 2-*tert*-butyliminomethylphenol, and its Co(II), Cu(II), Zn(II) and Pd(II) complexes [18]. Then, we have demonstrated the effectiveness of these complexes as catalysts for the green oxidation of sulfides to the corresponding sulfones with hydrogen peroxide. In this system, the reactions can be carried out under solvent-free conditions as a green

sustainable method using all the catalysts in the presence of H_2O_2 . Conversions of 20–96%, and selectivities of 98–100% for sulfones are observed with the four compounds as catalysts (Table 5, entries 27–32). The Zn(II) Schiff base complex shows a better catalytic activity for the oxidation of sulfide and the Co(II) Schiff base complex shows a lower catalytic performance under these reaction conditions. Our study indicated that Pd(II) Schiff base complex is able to convert thioanisole to the corresponding sulfone with mild conversion (74%) and high selectivity (99%) (Table 5, entry 29) [18].

So, in comparison with the above catalysts, the present Pd Schiff base catalyst, Pd_2LCl_4 (4), provides a desirable catalytic activity for the oxidation of sulfides to corresponding sulfone compounds than other Schiff base complexes. Although the ability of this Pd(II) Schiff base complex, Pd_2LCl_4 (4), in oxidation of sulfides to sulfones is similar to that of our previously reported Pd Schiff base complex derived from 2-*tert*-butyliminomethylphenol, PdL_2 [18], the catalyst recyclability and stability of our new Schiff base complex, Pd_2LCl_4 (4), are much better than those of our previously reported Pd Schiff base complex, PdL_2 , and it can be used several times without any obvious loss in activity.

4. Conclusion

In this study, four new Schiff base complexes, $\text{CoL}(\text{NO}_3)_2$ (1), NiLCl_2 (2), $\text{ZnL}(\text{NO}_3)_2$ (3) and Pd_2LCl_4 (4), have been prepared by the condensation reaction of 1,2-bis(2'-aminophenoxy)benzene with 2-pyridinecarbaldehyde in the presence of Co, Ni, Zn and Pd metal ions. All complexes have been characterized by IR and XRD spectroscopy techniques and elemental analysis. The synthesized complexes have very poor solubility in all polar and non-polar solvents such as: H_2O , MeOH, EtOH, CH_3CN , DMSO, DMF, CHCl_3 , CH_2Cl_2 , THF, etc. This parameter (insolubility) causes these complexes to be suitable for acting as heterogeneous catalysts without any organic/inorganic support. Catalytic performance of the complexes was studied in oxidation of thioanisole using hydrogen peroxide (H_2O_2) as the oxidant.

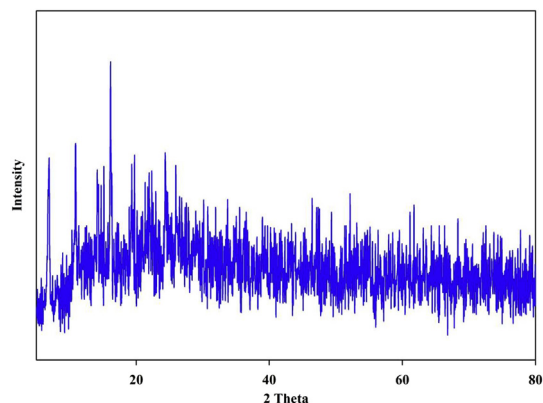


Fig. 5. XRD pattern of the Pd Schiff base complex recovered in run 5.

Table 5
Catalytic activity of various catalysts for the oxidation of sulfides.

Entry	Catalyst	Substrate	Solvent	Sulfoxide Conv(%) / Selec(%)	Sulfone Conv(%) / Selec(%)	Ref.
1	[3,3',5,5'-Cl ₄ salophen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	96/100		[26]
2	[5,5'-Cl ₂ salophen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	94/100		[26]
3	[salophen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	100/100		[26]
4	[5,5'-(<i>t</i> -Bu) ₂ salophen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	53/100		[26]
5	[3,3'-(OMe) ₂ salophen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	96/100		[26]
6	[5,5'-(OMe) ₂ salophen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	62/100		[26]
7	[3,3',5,5'-(<i>t</i> -Bu) ₄ salophen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	6/100		[26]
8	[3,3',5,5'-Cl ₄ salen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	35/100		[26]
9	[5,5'-Cl ₂ salen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	99/100		[26]
10	[salen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	15/100		[26]
11	[5,5'-(<i>t</i> -Bu) ₂ salen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	98/100		[26]
12	[3,3'-(OMe) ₂ salen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	>99/100		[26]
13	[5,5'-(OMe) ₂ salen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	93/100		[26]
14	[3,3',5,5'-(<i>t</i> -Bu) ₄ salen ^V O].CF ₃ SO ₃	PhSCH ₃	MeCN	98/100		[26]
15	PS-TETA-Co (with polymer support)	PhSPh	MeCN	90/100		[27]
16	(CoL)Cl ₄ H ₂ O (without support)	PhSPh	MeCN	76/100		[27]
17	PS-TETA-Co (with polymer support)	PhSC ₂ H ₅	MeCN	89/100		[27]
18	(CoL)Cl ₄ H ₂ O (without support)	PhSC ₂ H ₅	MeCN	73/100		[27]
19	[MoO ₂ (L)(CH ₃ OH)]	PhSPh	C ₂ H ₅ OH	75/93	75/7	[28]
20	[MoO ₂ (L)(CH ₃ OH)]	PhSPh	C ₂ H ₅ OH	95/3	95/97	[28]
21	[MoO ₂ (L)(CH ₃ OH)]	PhSCH ₃	C ₂ H ₅ OH	92/100	92/0	[28]
22	[MoO ₂ (L)(CH ₃ OH)]	PhSCH ₃	C ₂ H ₅ OH	100/2	100/98	[28]
23	Copper–Schiff base	PhSCH ₃	MeCN	100/82		[10]
24	Copper–Schiff base	PhSPh	MeCN	100/92		[10]
25	FeL ₂ (OAc)	PhSCH(CH ₃)	CH ₂ Cl ₂	100/94.6		[29]
26	Fe(salen)-MOF	PhSCH(CH ₃)	CH ₂ Cl ₂	94/100		[29]
27	CuL ₂ Schiff base complex	PhSCH ₃	Solvent-free		80/99	[18]
28	ZnL ₂ Schiff base complex	PhSCH ₃	Solvent-free		93/99	[18]
29	PdL ₂ Schiff base complex	PhSCH ₃	Solvent-free		74/99	[18]
30	CuL ₂ Schiff base complex	PhSPh	Solvent-free		83/99	[18]
31	ZnL ₂ Schiff base complex	PhSPh	Solvent-free		96/99	[18]
32	PdL ₂ Schiff base complex	PhSPh	Solvent-free		79/99	[18]
33	Pd Schiff base	PhSPh	MeCN		72/99	Present work
34	Pd Schiff base	PhSCH ₃	MeCN		70/99	Present work

Various factors including the reaction temperature, amount of oxidant and catalyst amount were optimized. Among the four Schiff base complexes, the Pd(II) Schiff base complex, **Pd₂LCl₄ (4)**, showed better catalytic activity in oxidation of thioanisole compared to methyl phenyl sulfone. Therefore, the Pd(II) Schiff base complex has been used as the catalyst for oxidation of different sulfides to the corresponding

sulfones in acetonitrile using hydrogen peroxide as the oxidant. The Pd(II) complex, **Pd₂LCl₄ (4)**, showed high activity with good selectivity for the oxidation of various sulfides. This separable catalyst can be prepared by a very simple procedure, by filtration, and the catalyst can be reused for five cycles without any significant changes in its catalytic activity and structure.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.crci.2015.10.003>.

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