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Hydrogen peroxide oxidation of primary alcohols by thiosemicarbazide Schiff base metal complexes

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ABSTRACT

A series of transition metal complexes with two thiosemicarbazide Schiff bases, 1-(4-dimethylaminobenzyl-idene)thiosemicarbazide (ABTSC) and 1-(2-pyridincarboxyl-idene) thiosemicarbazide (TCTS) were synthesized with Co(II), Ni(II), Zn(II), Cd(II) and Ag(I) salts (chloride and acetate). These complexes were characterized by different methods including proton nuclear magnetic resonance (1HNMR), Fourier transform infrared (FT-IR), ultra violet visible (UV-Vis), molar conductance (λm), atomic absorption spectroscopy (AAS) and elemental analysis (CHNS). All complexes were applied as a catalyst for oxidation of aromatic alcohols. The effects of reaction time, temperature, catalyst amount, oxidant and solvents were investigated in detail. The oxidation of alcohols occurs effectively and selectively with H2O2 as the oxidant. For instance, 4-Methoxybenzyl alcohol is oxidized to the corresponding aldehyde with 95% conversion and 100 % benzaldehyde selectivity under the optimum conditions.

Keywords: *Alcohol oxidation; Thiosemicarbazide; Schiff base metal(II)complex.*

1. Introduction

Alcohol oxidation process to the corresponding carbonyl compound is essential for preparation of many organic intermediates, aldehydes, fragrances, pharmaceuticals, agricultural chemicals and food additives [1-6]. Oxidation of alcohols has long been carried out in environmentally harmful organic solvents at high pressure and temperature by employing stoichiometric amounts of various inorganic oxidants which led to the formation of unfriendly by-products [7].

Efficient homogeneous catalysts based on ruthenium [8-11], cobalt [8,9], palladium [10-16], copper [17,18] in the process of alcohol oxidation have been reported. Regarding the heterogeneous metal catalysts, mostly gold-palladium [19-21], gold [22], platinum [23] and silver [24] in the forms of nanoparticles, clusters or complexes have been studied as oxidation catalysts. In these articles, the catalyst comprised of a central metal atom and the surrounding organic ligand(s) as well as polyoxometalates typically oxides of molybdenum, tungsten and vanadium are applied for effective oxidation of alcohols [25,26]. For the gas phase oxidation of alcohols, the suitability of heterogeneous silver catalysts is considered to be the most fit [27,28]. Recently, the applications of monometallic and bimetallic gold based catalysts in the liquid phase of alcohol oxidation were explored in a successful manner [29,30].

The demand for developing a cost effective and environmentally-friendly process for oxidation of the alcohol with high selectivity and yield of product is on increase. The commonly used oxidants like Cr(IV), potassium permanganate (in acidic, basic and neutral solution), bromine and nitric acid are not suitable for the aldehyde oxidation due to the condition they require to be effective or the side products they produce after oxidation. Some of these oxidants need high acid concentrations for which it is very difficult to undertake reactions in milder conditions for acid sensitive compounds. Insolubility of oxidants in non-aqueous solvents, formation of large amounts of liquid and hazardous solid wastes and the corrosive nature of the reaction medium are some other problems with common oxidants which make oxidation process tedious for water insoluble organic substrates. Halochromates are another group of oxidants which have a long shelf life and better solubility in organic

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solvents but the carcinogenicity of chromium especially when is used in excess amounts. In light of this, there is a need for environmentally friendlier oxidation reactions that retain the power of chromium oxidants [31,32].

The transition metal Schiff base complexes have drawn much attention in the catalysis process due to their more accessible synthesis conditions, versatile structural coordination and also their reusability in the process [20,33]. In this context, the Schiff bases prepared through condensation of thiosemicarbazide with suitable aldehydes, not only can behave as unidentate ligands and bond through only sulphur atoms [34], but also they are able to behave as bidentate ligands and bond to metals through sulphur and the hydrazine nitrogen atoms [35]. Thiosemicarbazide Schiff base derivatives have considerable antibacterial, antimalarial, antiviral and antitumor activities [36]. Complexions of such thiosemicarbazide ligands with metal ions are found to produce synergistic effects on antiproliferative activities of the parent ligands. In this article, a series of metal complexes of two thiosemicarbazide Schiff bases with 4-dimethylaminobenzaldehyde and 2-pyridinecarbaldehyde have been synthesized. The catalysts are prepared by 1-(4-dimethylaminobenzyl-idene) thiosemicarbazide (ABTSC) and 1-(2-pyridincarboxyl-idene) thiosemicarbazide (TCTS) Schiff bases and Co(II), Ni(II), Zn(II) and Cd(II) salts (chloride and acetate). Fig. 1 shows structures of the Schiff base ligands used in this study. The influence of the reaction temperature, solvents, amount of catalysts and concentration hydrogen peroxide on the oxidation process is investigated as well.The simple synthesis of the catalysts, the neutral and nontoxic condition for the transformation of alcohols to aldehydes, the reusability of the catalysts for the next cycles as well as their short time and high oxidation yield are among the major findings in this research (Scheme 1).

2. Experimental

2.1. General

All the chemicals used in the synthesis were of reagent grade and were used without further purification. ^{1}HNMR spectra were recorded on Bruker DPX400 NMR Spectrometer, infrared spectra (400–4000 cm^{-1}) were recorded on KBr pellets on a PerkinElmer Spectrum 65 spectrometer.

$$RCH_2OH \xrightarrow[\text{rt, } H_2O_2 \text{ (3 mmol)}]{\text{Ctalyst (0.03 mmol)}} RCHO$$

Scheme 1. Oxidation of Alcohols by hydrogen peroxide catalyzed by M(L).

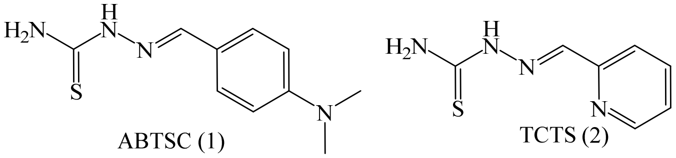


Fig. 1. Structure of 1-(4-dimethylaminobenzylidene) thiosemicarbazide (1), 1-(2-Pyridine carboxylidene) thiosemicarbazide (2).

The metal contents measured by absorption spectra were recorded by applying Analyst 300, Perkin Elmer Co. USA spectrophotometer. Elemental analyses were carried out on a CHNS analyzer, CHNS-932, Leco and USA elemental analyzer. Melting points were determined on an Electro Thermal IA 900 apparatus. The molar conductance obtained by a DDS-11A conductometer. The electronic spectra were obtained by UV-Vis methods with a PG Instruments T70 spectrophotometer.

2.2. Ligand Synthesis

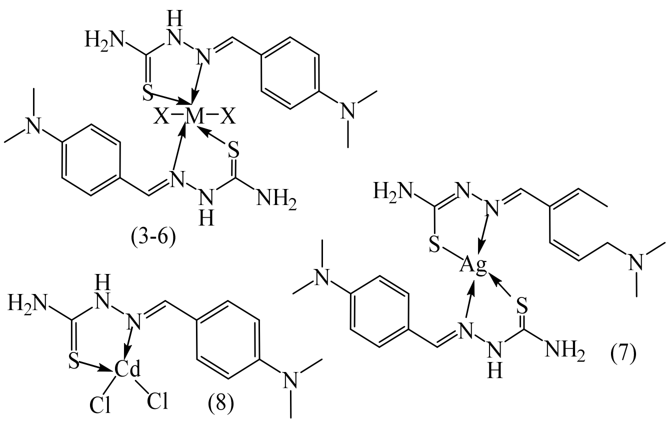
The ABTSC and TCTS Schiff bases have been synthesized based on the published procedure [37-38].

2.3. Complex Synthesis with Schiff base

All complexes were prepared in a similar manner. Two synthesis procedures, as an example are given below.

For complex synthesis with Schiff base a MeOH solution (10 ml) of 1(0.44 g, 2 mmol) was added to a MeOH solution (20 ml) of metal salts [$M(X)_2 \cdot nH_2O$] (1 mmol) 40°C and stirred for 10 min at room temperature and then refluxed for 5 hours. The reaction progress was monitored by TLC. The solid was then filtered, recrystallized in ethanol at 40 °C and dried under reduced pressure for 9 hours, to isolate a colored solid. (Fig. 2).

For synthesis of [$M(TCTS)_2$]X_2 (9-12), compound 2 (0.361 g, 2 mmol) in 40 ml of methanol/ethanol was



M= Ni, X=OAc (3); Zn, X=OAc (4); Co, X=OAc (5), Cl (6)

Fig. 2. Proposed structures for ABTSC metal(II)complexes.

added to an ethanol solution (10 ml) of metal salts $[M(X)_n \cdot nH_2O]$ (1 mmol) and was refluxed for 5 hours in which a precipitate was formed at low temperature. The reaction progress was monitored by TLC. The solid was then filtered and recrystallized in ethanol to isolate a colored solid, "9-12". Physical data of complex is shown in Table 1, (Fig. 3). For preparation of complexes (9-12) the amount of $[M(X)_2 \cdot nH_2O]$ and reaction time is as follows: $CuCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol), with $NiCl_2.6H_2O$ (0.238 g, 1 mmol), with $AgNO_3$ (0.16 g, 1 mmol) and with $CdCl_2.H_2O$ (0.40 g, 2 mmol) (Fig. 3).

2.4. Oxidation of alcohols

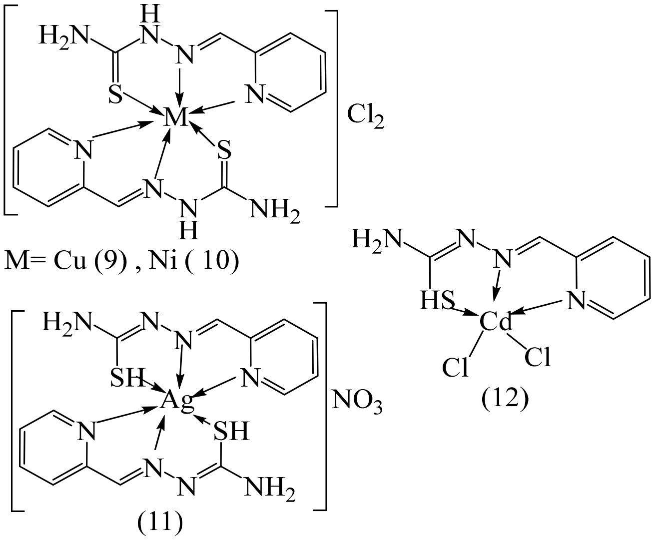
A mixture of catalyst 0.03 mmol and 0.08 ml of 30% hydrogen (3 mmol) peroxide were added slowly into 3 ml CH_3CN and followed by 1 mmol benzyl alcohol into a 50 ml flask fitted with a reflux condenser and magnetic stirrer. The reactor containing this mixture was refluxed in an oil bath with electric heater. The resulting mixture was stirred by a magnetic stirrer for 80 min. At the end of the reaction, the solution including the catalyst and the corresponding aldehydes were extracted by benzene for three times. All the isolated carbonyl compounds are commercially available and were identified by a comparison of their gas chromatography (GC) and infrared spectroscopy (IR) with data from authentic samples in the literature. The catalyst solution was evaporated in vacuum at 70°C and further washed with absolute ethanol and diluted water, then dried at 70°C in a vacuum oven for recovery of the catalyst.

2.5. Reusability of the catalyst

At the end of each reaction, the solution was cooled down to room temperature and was washed with chloroform to furnish analytically pure product with >95% recovery in all cases.

3. Results and Discussion

All the complexes were obtained as solids by the reaction of ligands with metal salts. The elemental analysis of the ligands and their metal complexes are in good agreement with the calculated data (Table 1). The metal(II) complexes of thiosemicarbazide Schiff bases (ABTSC and TCTS) of the type $[M(ABTSC)_2X_2]$ (M= Co, X= Cl, OAc, M= Ni, X= Cl, M= Ag, X= NO^{3-}, M= Zn, X= Cl), $[Cd(ABTSC)Cl_2]$, $[M(TCTS)_2]Cl_2$ (M= Cu, Ni, Co) and $[Cd(TCTS)]Cl_2$ have been prepared from the reaction of the Schiff bases with the corresponding metal salts in 1:1 or 2:1of L:M ratios (Fig. 2-3). The analytical data of the new complexes (Table 1) are in good agreement with the proposedmolecular formulas. The percentage yield of the product ranges from 65 to 80%.



M= Cu (9) , Ni (10)

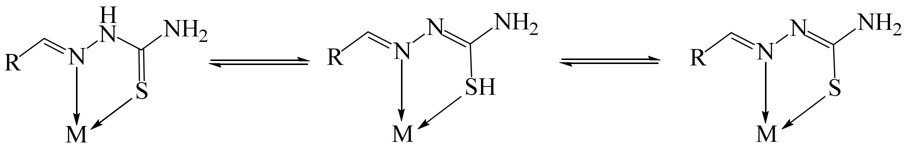
(11)

(12)

Fig. 3. Proposed structures for metal(II) complexes with TCTS.

All complexes have been characterized with different methods. Synthesis of Schiff base complexes have been examined with different anions of chloride, acetate and nitrate. The role of the anion accompanying the complex appears by its participation in the first coordination sphere of metal ion. This role is mainly controlled by the structure of the complex and the coordinating nature of the anion, as well [39]. Surprisingly, these two Schiff bases have different binding modes for the same transition metals. The molar conductivities of the compounds 3-8 and 12 (12-25 Ω-1cm2mol-1) indicate that the coordination of anion and the ligands to the central metal which results non-electrolyte compounds. However, the molar conductivity values of compounds 9-11 suggest that they are electrolytes [35] (Table 1). The Schiff bases, ABTSC and TCTS have two similar coordination sites, azomethine nitrogen and thiol/tionsulphur atoms. Due to these two coordination sites, the ABTSC behaves as bidentate ligand40. However, in the case of TCTS, the presence of extra coordination site (2-pyridine carbaldehyde moiety) causes the Schiff base to coordinate as tridentate ligand (N,N,S-donor) and force the anion of the metal salt to use the outer coordination sphere of the complex. For both ligands, existence of thiosemi moiety provides situations for transformation into the thiol form.

The state of tautomerism is determined by the ability of the aryl groups to conjugate, and in addition the stability of the intermediate tautomer by electron donation/withdrawal of the anion as well as the electron density of the metal center (Scheme 2). In this process, the possibility of dissociation of the acidic proton and the formation of complex with anionic ligand are provided (Scheme 2) [41].



Scheme 2. General tautomerize forms of thiol/thion forms of thiosemicarbazide complexes.

3.1. FT-IR spectra

The FT-IR spectra of the free ligands were compared with the spectra of the prepared complexes in order to study the binding mode of the Schiff bases to the metal centers in these new complexes. Strong bands are observed at 1608 and 1609 cm^{-1} in the infrared spectra of the free Schiff bases (ABTSC and TCTS) which are characteristic of the azomethine group respectively. If the Schiff bases coordinate through the nitrogen atom, a reduction is expected in the azomethine frequency of all the complexes, due to the lowering of electron density upon coordination. In the spectra of all the new complexes, this band is shifted to the 1547–1600 cm^{-1} region, indicating the coordination of the Schiff bases through nitrogen atom (Table 2) [1]. The strong bands observed in the area of ≈ 870 cm^{-1} and ≈ 1200 cm^{-1} were due to the δ(C=S) and ν(C=S) vibrations [19]. The ν(C=S) stretching frequencies were lowered in the spectra of all complexes, indicating the involvement of the thiol/tion sulphur in the coordination to the metal centers. The bands observed at 3416-3377 cm^{-1} were assigned to ν(N-H) asymmetric vibrations of NH_2 and symmetric vibrations of NH in thiosemi moiety in these Schiff bases [1]. In these complexes, the N-H bands shift to both higher and lower energies, suggesting the references in hydrogen bonding of NH [20]. Strong bands found at 1111–1174 cm^{-1} in the ligands are assigned to the ν(N–N) band of the thiosemicarbazide. The increase in the frequency of these bands in the spectra of complexes is due to the increase in the bond strength, confirming the coordination through the azomethine nitrogen [22].

The complex containing the anionic ligand (7) or those in which the thiol form, are preferred over thion form (11, 12) [10, 33] a second band is often resolved due to ν(N=C) and the ν(N-H) vibration disappears in the spectra of complexes, except 7, 11 and 12, providing a strong evidence for the ligand coordination around metal(II) ion in the deprotonated or thiol form19. The presence of the bands in 402–415 cm^{-1} range is assigned to ν(M–N) which is in good agreement with previous studies conducted on metal complexes of 2-formylpyridine N(4)-substituted by thiosemi carbazones [21].

The FT-IR spectral data of ligand and all the complexes are shown in Table 2.

Table 1. Physical characterization and analytical data of the prepared complexes (3-12).

Compound	C%		H%		N%		S%		M%		λ_m
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	($\Omega^{-1}cm^2mol^{-1}$)
3	46.05	46.40	5.10	5.47	17.85	18.04	10.08	10.32	9.80	9.45	22
4	41.15	41.30	4.20	4.82	19.05	19.30	11.20	11.04	11.83	11.26	18
5	46.05	46.37	5.10	5.51	17.80	18.03	10.05	10.32	9.64	9.48	25
6	41.30	41.82	4.30	4.91	19.10	19.51	11.05	11.17	10.82	10.26	16
7	43.20	43.56	5.30	4.93	20.70	20.27	11.10	11.58	20.14	19.56	14
8	28.01	28.42	3.20	3.76	13.05	13.17	7.10	7.53	26.70	26.60	12
9	33.66	33.97	3.26	3.26	22.64	22.65	11.95	12.95	13.67	12.83	43
10	31.60	31.96	3.50	3.83	21.10	21.30	12.20	12.19	10.42	11.15	48
11	29.43	29.68	3.49	3.55	22.13	22.26	11.18	11.32	19.04	19.58	36
12	20.73	21.03	2.48	3.03	13.78	14.02	8.00	8.02	27.913	28.13	25

Table 2. FT-IR data of the prepared complexes and ligands.

Compound	IR (cm^{-1})			
	ν (C=N)	ν (N-N)	ν (C=S)	ν (M-N)
1	1608	1082	1230, 811	-
2	1567	1061	1224, 852	510
3	1600	1047	1244, 814	523
4	1578	1029	1223, 851	517
5	1599	1168	1226, 817	561
6	1680, 1594	1035	1286, 873	522
7	1597	1057	1293, 803	520
8	1609	1111	1294, 875	-
9	1583	1169	1227, 877	565
10	1547	1163	1228, 881	515
11	1639, 1555	1156	1293, 878	516
12	1620, 1584	1173	1231, 881	511

3.2. UV-Vis spectra

The electronic spectra of the ligands and metal complexes in CH_3OH were recorded in 200–800 nm range. The intense absorption bands observed in the 237-247 nm and 325-376 nm are related to π→π* and n→π* of aromatic ring and azomethine group respectively. As usual, the absorption bands observed in 400-766 nm range, most likely arise from a d–d transition of metal centers of these complexes. The electronic spectra data of the prepared compounds are reported in Table 3 [42].

3.3. ^{1}HNMR spectra

The ^{1}HNMR spectra of the metal complexes with two thiosemicarbazide Schiff bases, 1-(4-dimethylamino benzylidene) thiosemicarbazide (ABTSC) and 1-(2-pyridincarboxyl-idene) thiosemicarbazide (TCTS) in DMSO solutions with their assignments are presented in Table 4. The Pyridine proton signals of TCTS in ^{1}HNMR spectra appear at 7.37-8.56 ppm (4H, m), the azomethine proton at 8.56 ppm (1H, s), secondary amine proton at 11.65 ppm (1H, s) and proton signals at 8, 8.19 ppm are related to NH_2 (2H, s).

In the ^{1}HNMR spectrum of compound 10, the hydrogen signal of azomethine shifted the low field whereas the aliphatic hydrogens of the methyl group have shifted the up field. The ^{1}HNMR spectrum of complex 7 exhibits the aromatic NMR spectrum of complex 4, confirms the presence of two non-equivalent ligand molecules [7].

3.4. Catalytic activities of compound 3-12

The catalytic activities of the complexes in the oxidation of benzyl alcohol were tested in the presence of hydrogen peroxide as oxidant and CH_3CN as solvent. The yield of oxidation reaction in the absence of catalysts is very low. All the synthesized Schiff base complexes were found to catalyze the oxidation of alcohol to aldehydes in which the yield and the turnover were found to vary with different catalysts used (Fig. 4, Table 4-5).

3.5. Effect of reaction conditions

The oxidation of benzyl alcohol derivatives was studied based on the varying temperature, the amount of catalysts, the amount of oxidant and the type of solvents. In order to investigate the effect of temperature of this catalytic system, the catalytic reactions were run at different temperatures by employing 0.03 g of 5 for 1 mmol BzOH. At room temperatures no significant conversion was noted. Raising the temperature to 82°C led to a consistent enhancement in the conversion. The changes in the product conversion with temperature are shown in Table 5.

Table 3. UV-Vis data of the prepared complexes and ligands.

Compound	UV/Vis λ_{max} (ε), nm (mol^{-1} cm^{-1})
1	247(651),347(330)
2	241(3865), 368(2768), 475(1785), 766(1326)
3	237(7852), 353(4056)
4	237(3562),376(2854), 672(1650), 596(1750)
5	237(3879),362(2950), 598(1905), 672(1570)
6	220(4696), 325(3065)
7	237(6590), 360(3852)
8	236(758), 268(482), 325(340)
9	324(7410), 409(4271), 616(2842)
10	219(7510), 300(5942), 360(3725), 404(1642), 528(1362), 595(1070)
11	220(5673), 325(3458)
12	263(5410), 320(3261), 322(3123), 378(3045)

The optimum reaction temperature for the highest BzH conversion is 82°C whereas the selectivity for BzH has almost remained unchanged. At higher temperature, the selectivity decreases and substantial amounts of other products like benzoic acid is produced. This finding indicates a rise in temperature (82 °C) could accelerate the oxidation reaction and has almost no impact on the selectivity. Thus, the selective oxidation reaction for BzOH conversion with high selectivity (for BzH) occurs at higher temperatures. The effect of catalyst amount on the oxidation of benzyl alcohol was studied by increasing the catalyst amount from 0.01g to 0.1 g, as shown in Table 5.The results indicate that the conversion of BzOH increase with an increase in the amount of catalyst. The maximum conversion was obtained when 0.03 g of the catalyst was used.

The excess amount of the catalyst decreased the selectivity for BzH, which was likely attributed to further BzOH oxidation into the byproducts (e.g. toluene, benzene and benzyl benzoate) catalyzed by the excess amount of Lewis acidity sites or decomposition of the hydrogen peroxide [37]. Another important factor in oxidation and its yield was the type of solvent in which the oxidation happened. It is clear that protic solvent due to the strong interaction with catalyst surface are not suitable for the oxidation. Polar protic solvent competes with the hydroxyl of the alcohol for reaction with catalyst and lowers the efficiency of the reaction. Polar aprotic solvent due to having less interaction with the catalyst surface delays catalyst inactivity for oxidation. The effect of H_2O_2 amount on the oxidation of BzOH into BzH was investigated (Table 5). The conversion increased with increasing the molar ratio of H_2O_2/BzOH.

The maximum conversion of BzOH to BzH obtained when the molar ratio of oxidant/alcohol reached at 3/1, afterwards as the ratio increased, the yield declined slightly. According to stoichiometry, one mole of H_2O_2 is required for the oxidation of one mole of BzOH into BzH. The excess amount of H_2O_2 is required due to its

Table 4. ^{1}HNMR spectra (DMSO-d_6) of the thiosemicarbazide metal(II) Complexes.

Compound	N-H	NH_2	CH=N	Ar/(Py)	CH_3
1	11.65	8 (2H), 8.19(2H)	8.38(2H)	----	----
2	11.2(2H)	8(2H), 7.7(2H)	7.9(2H)	7.5(4H),6.7(4H)	3.3(6H), 2.9(6H)
3	11.8(1H)	8.49(4H)	8.0(2H)	7.66(4H, 6.75(4H)	3(12H)
4	9.7(2H)	8.1(4H)	8.6(2H)	7.9, 7.5, 7.3, 6.8(8H)	-----

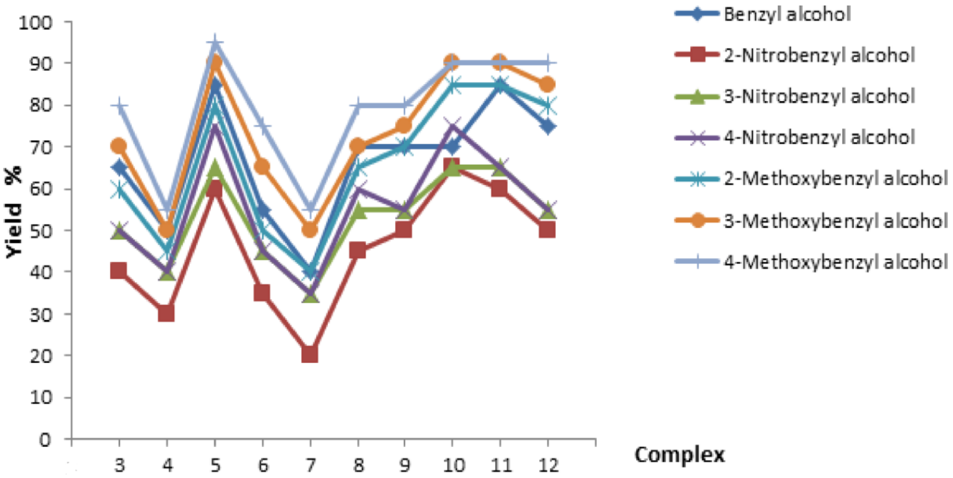


Fig. 4. Oxidation yield presentation of complexes 3-12 for different benzyl alcohols.

decomposition either at the elevated temperature or in the presence of the catalysts. The oxygen released in the decomposition reaction plays no role in the oxidation of alcohols. No oxidation occurred under similar conditions by using oxygen as oxidant.

To assess the scope of the reaction, the oxidation of other benzylic alcohols was then examined using the optimized reaction conditions (catalyst, 0.03 mmol, benzyl alcohol, 1 mmol, oxidant, 3.0 mmol, in CH_3CN, 3 ml, 80 minutes, 355 K, Table 6). Among the catalysts used in this study, $[Co(ABTSC)_2(OAc)_2]$ (5) has generated the best results which are presented in Fig. 4.

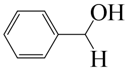
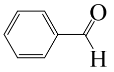
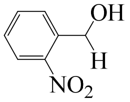
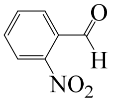
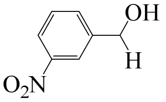
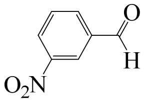
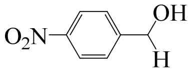
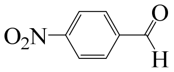
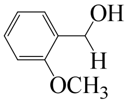
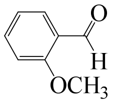
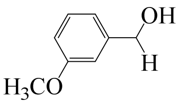
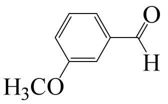
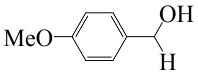
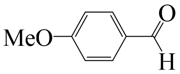
4. Conclusions

In summary the catalytic activity of thiosemicarbazide Schiff base complexes are eco-friendly and efficient heterogeneous catalyst for the selective oxidation of benzylic alcohols is explored. The catalysts exhibit high activities in all runs without any appreciable loss in activity, which is an environmentally friendly

Table 5. The Optimization of Benzyl Alcohol with compound 5.

Entry	Catalyst (mmol)	Oxidant (mmol)	Temp. (°C)	Solvent	Yield (%)
1	0.0	1.0	25	Ethyl acetate	15
2	0.0	2.0	25	Ethyl acetate	20
3	0.0	3.0	25	Ethyl acetate	20
4	0.0	2.0	25	Chloroform	20
5	0.0	3.0	25	Chloroform	25
6	0.0	2.0	25	Hexane	25
7	0.0	3.0	25	Hexane	25
8	0.0	3.0	25	Acetonitrile	25
9	0.01	3.0	25	Acetonitrile	50
10	0.01	3.0	40	Acetonitrile	55
11	0.02	3.0	50	Acetonitrile	60
12	0.03	3.0	50	Acetonitrile	60
13	0.03	3.0	60	Acetonitrile	65
14	0.03	3.0	70	Acetonitrile	70
15	0.03	3.0	82	Acetonitrile	85
16	0.03	4.0	82	Acetonitrile	85
17	0.1	3.0	82	Acetonitrile	85

Table 6. Oxidation benzyl alcohol derivatives for complex [$Co(ABTSC)_2(OAc)_2$]^a.

Compound	substrate	Product	Selectivity (%)	Yield (%)
1			100	85
2			97	65
3			97	65
4			100	75
5			100	85
6			100	90
7			100	95

^{a} Reaction conditions: catalyst (0.03 mmol), benzyl alcohol (1 mmol), oxidant (3.0 mmol), in CH_3CN (3 ml), 80 minutes, 355 K.

oxidation system. In the catalytic process, many factors including the reaction temperature, the type of solvent, the amount of catalyst and the oxidant have an evident influence on the catalytic oxidation activity and selectivity. A 95 % conversion of 4-Methoxybenzyl alcohol with 100 % benzaldehyde selectivity was achieved under the following optimum conditions: reaction temperature of 355 K, reaction time of 80 min, with 3 ml of CH_3CN and 3/1 mmol ratio of oxidant to catalyst, making these catalysts and their conditions very economically feasible to be used for alcohol oxidation.

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