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Synthesis, Characterization, and Biological Activity of Chromium Complexes as Efficient and Novel Catalysts for Direct Synthesis of Carbonyl Compounds from Benzyl/Cycloalkyl Bromides in Water under Aerobic Oxidation

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ABSTRACT

The oxidation process of benzylic halides especially benzylic bromide to corresponding carbonyl compounds such as aldehydes and ketones is a worthwhile and important organic reaction in industrial and laboratory synthetic organic chemistry. In the present study, an efficient and novel method to obtain carbonyl compounds using benzyl bromide with a catalytic amount of chromium complexes in water under aerobic conditions was reported. The six types of chromium complexes were prepared via the reaction mixture of four ligands. The prepared ligands and chromium complexes were characterized using Fourier transform spectroscopy (FT-IR), elemental analysis, molar conductivity, and magnetic moment, as well as UV-Vis spectroscopy. Different benzyl bromide derivatives were selected with both electron-donating groups and electron-withdrawing groups at –*ortho*, -*meta*, and –*para* positions. Under the optimum conditions, the corresponding benzaldehyde derivatives were obtained in moderate to excellent yields. In addition, the biological activity of the prepared chromium complexes was checked.

Keywords*: Carbonyl compound, Chromium complex, Oxidation, Synthesis, Biological activity*

1. Introduction

The oxidation process of benzylic halides especially benzylic bromide to corresponding carbonyl compounds such as aldehydes and ketones is a worthwhile and important organic reaction in industrial and laboratory synthetic organic chemistry [1, 2]. In many cases, the oxidation of benzylic halides to carbonyl compounds such as aldehydes and ketones is more efficient and convenient than the oxidation of alcohols to corresponding carbonyl compounds. Recently, there are many research groups developed the conversion of benzylic halide (bromide) to aldehyde compounds. **Scheme 1** shows different routes for the preparation of carbonyl compounds in three parts. Recently, the complexation of transition metals such as Cr, Fe, V, Mn, Co, Ni, and Pd is attractive in organic reactions [13]. Several metals can be combined with different ligands. Chromium complexes are mostly synthesized by the treatment of convenient molar ratio of ligand and source of chromium metal such as $Cr(CO)_6$ and $CrCl_3.6H_2O$. Different research groups synthesized chromium complex and used organic reaction including oxidation [14], reduction [15], polymerization [16], and asymmetric reaction [17]. Some structures of different chromium complexes are shown in **Fig. 1**.

In this study, we prepared four different ligands including 2,2'-(hydrazine-1,2-diylidene)bis(1,2-diphenylethan-1-ol) (Benzoinazine-BAH2)(Ligand 1), (E)-2-((4-oxopentan-2 ylidene)amino)benzoic acid, (Acetylacetonemonoanthralidene-AA1H)(Ligand 2), 2,2'-(((2E,4E)-pentane-2,4 diylidene)bis(azaneylylidene))dibenzoic acid (Acetylacetonedianthralidene-AAH2)(Ligand 3), and (E)-4-((2-hydroxyphenyl)imino)pentan-2-one (Acetylacetonemonohhydroxyanilidene-AnH)(Ligand 4). Then, the pointed ligands were coordinated with $CrCl_3.6H_2O$ to afford the target chromium complexes. Then, the prepared chromium complexes are used in the direct synthesis of carbonyl compounds from benzylic bromide in water under aerobic oxidation.

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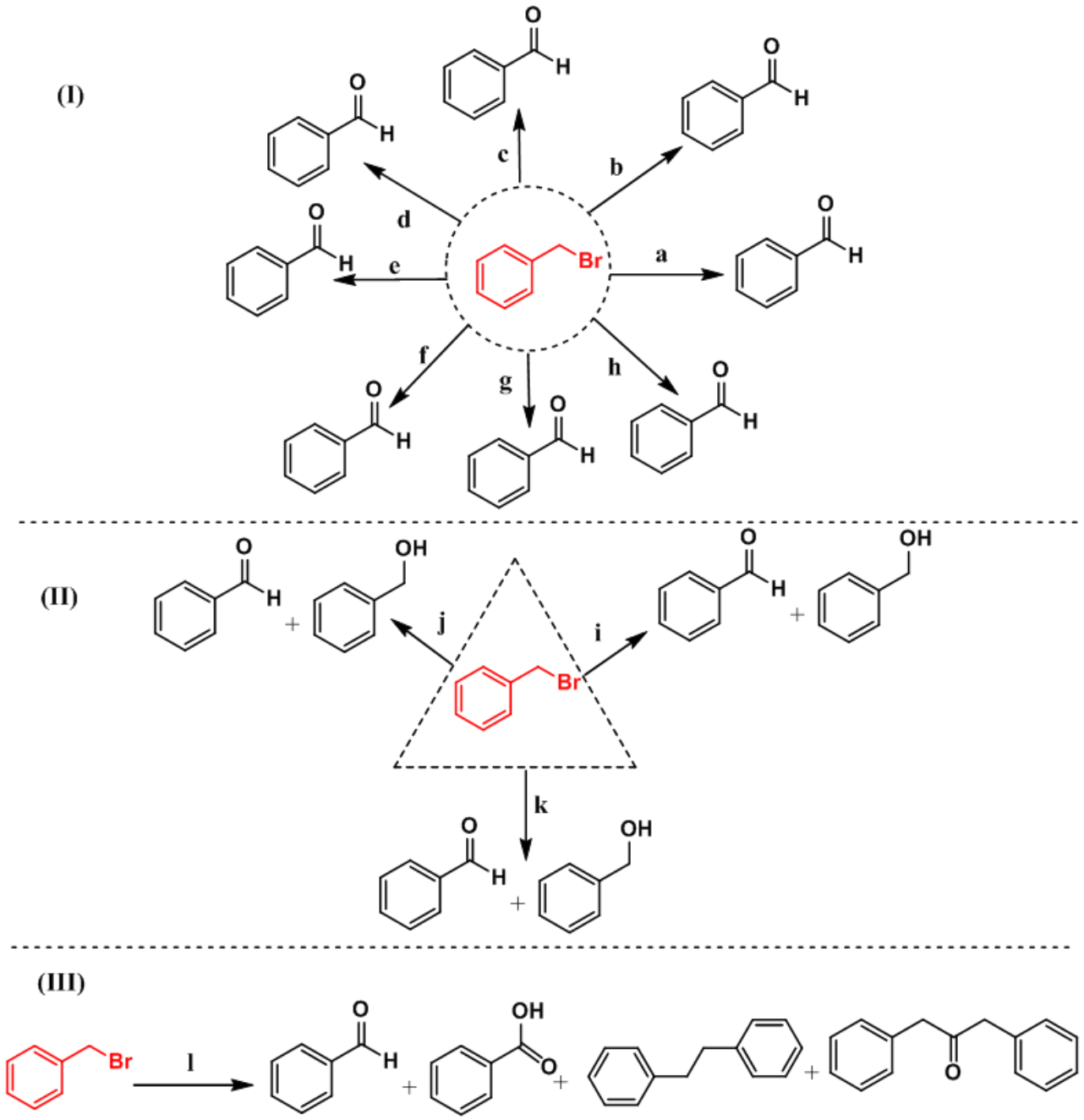


Scheme 1. Different routes for preparation of carbonyl compounds: PART (I): (a) H2O, NaOH, Time: 0.05 h, T: 20 □C, Microwave Irradiation, Yield: 99% [2]. (b): Potassium nitrite, 2.2.6.6-tetramethyl-1-pipiridenyloxy free radical, O2 in H2O, Time: 3.5 h, Reflux, Yield: 95% [3]. (c): 4-methylmorpholine N-oxide, 1-ethyl-3-methyl-1H-imidazole-3ium chloride, Time: 0.033 h, T: 100 □C, Microwave irradiation, ionic liquid, Yield: 95% [4]. (d): Bis(4-methoxy-phenyl)selenoxide, NaHCO3, THF, Time: 10 h, heating, Yield: 93% [5]. (e): KHCO3, DMSO, Time: 0.0416 h, Microwave irradiation, Kornblum oxidation, Yield: 93% [6]. (f): H2O. 1-hydroxy-3H-benzo[d][1,2]iodoxol-1,3-dione, Time: 0.33 h, T: 50 □C, ionic liquid, inert atmosphere, Yield: 92% [7]. (g): Stage 1: 2.2.6.6-tetramethyl-1-pipiridenyloxy free radical, O2 in H2O, Time: 3.5 h, Reflux, Stage 2: H2O2 in H2O, Time: 2h, Yield: 92% [8]. (h): Bismuth (III) nitrate pentahydrate, tetrabutyl ammonium fluoride, Time: 1h, T: 100 □C, Yield: 91% [9]. PART (II): (i): di-(p-methoxyphenyl)tellurium oxide in toluene, Heating, Yield: 6% and 90% [5]. (j): 1-methyl-4-nitrosobenzene, sodium acetate in dichloromethane, Time= 12h, T= 55 °C, Inert atmosphere, Yield: 40% and 12% [10]. (k): oxygen, triethylamine, sodium iodide in acetonitrile, Time= 24h, T= 32 °C, Schlenk technique, UV-irradiation, Yield: 27% and 35% [11]. PART (III): (l):sodium hydroxide, cobalt tricarbonyl nitrosyl, carbon monoxide, trimethyldodecylammonium chloride in benzene, p= 760Torr , Ambient temperature, Yield: 58%, 4%, 9%, 7% [12].

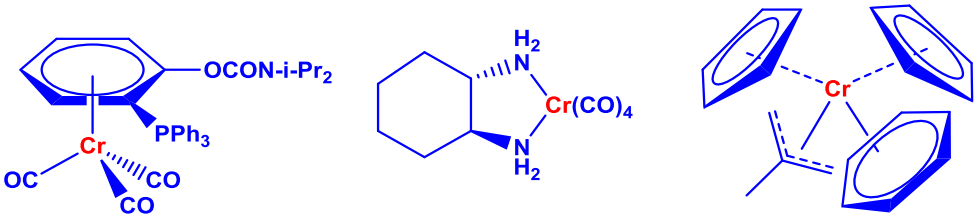


Fig. 1. Some chemical Structure of chromium complexes with both catalytic and biological activity.

2. Experimental

2.1. General

The solvent, chemical, and source of metals were purchased from Merck and Sigma-Aldrich chemical companies and used without further purification. The prepared complexes were analyzed using carbon, nitrogen, hydrogen (CHN), and chromium contents have been measured by atomic absorption spectroscopy after the decomposition of the complexes with concentrated nitric acid. The relative molecular weights of the ligands and their complexes have been theoretically determined. Molar refraction measurements have been carried out with Atago Illumination, Atago Co-LTD, Japan using 10^{-3} M dimethyl sulfoxide solution. The conductivity measurements has been carried out with an electrolytic conductivity measuring set LF-42 and Multiline F/SET-2WTW Wiscenschaf Tecchnische Werketattem 82362 Weiheim using 10^{-3} M dimethylsulfoxide at 25 ^{o}C. Magnetic susceptibility of the complexes has been measured by (SHERWOOD SCIENTIFIC Magnetic Susceptibility (MSB) at 25 ^{o}C. Electronic spectra have been recorded on Shimadzu UV-1650 PC UV-Visible Spectrophotometer for 10^{-3} and 10^{-4} M solutions of the ligands and their complexes in dimethyl sulfoxide at 25 ^{o}C, using a 1 cm cell. The infrared spectra of the ligands and their complexes have been recorded on Model Alpha–Bruker in the range 400-4000 cm^{-1}.

2.2. Typical procedure for the preparation of ligands

The following ligands have been prepared according to the reported literature [18]. Ligand 1: At first, in a canonical flask (100 mL), 10 mmol of benzoine and 5 mmol of hydrazine hydrate were stirred at 80 °C in ethanol medium. Then, the reaction mixture was cooled to room temperature and 5 mL of water was added. Finally, the obtained ligand was filtered and dried at 70 °C for 18 h. Ligand 2: For the preparation of the pointed ligand, initially, into a canonical flask (100 mL), 10 mmol of acetylacetone, and 10 mmol of 2-aminobenzoic acid were mixed at 80 °C in H_2O: EtOH (1:1) solvent. After completion of the reaction, the solid materials were washed thoroughly using water to afford pure ligand 2. For the preparation of ligand 3, the same procedure was employed with the molar ratio (1:2) of acetylacetone and 2-aminobenzoic acid. Ligand 4: Initially, in a canonical flask (100 mL), 10 mmol of acetylacetone and 10 mmol of 2-aminophenol were mixed at 80 °C in H_2O: EtOH (1:1) solvent. After completion of the reaction, the solid materials were washed thoroughly using water to afford pure ligand 4.

2.3. Typical procedure for the preparation of chromium complexes under neutral and basic conditions

In this study, the six chromium complexes were prepared in the neutral and basic medium as follows: Complex 1: A mixture of Ligand 1 (0.39 g): Ligand 2 (0.20 g): $CrCl_3.6H_2O$ (1:1:1) was dissolved and heated in a small amount of water and ethanol for 3 h. Then, the reaction mixture was cooled to room temperature. Finally, the solid chromium complex (1) was washed thoroughly with diethyl ether and dried at 50 °C. Other complexes (complexes 3 and 5) were prepared under the same method. Complex 2: A mixture of Ligand 1 (0.39 g): Ligand 2 (0.20 g): $CrCl_3.6H_2O$ (1:1:1) was dissolved and heated in a small amount of water and ethanol for 3 h. The mixture was heated until a clear solution has been obtained. The aqueous solution of sodium hydroxide (2 M) has been added dropwise to the mixture until pH= 9-10 was obtained. Then, the reaction mixture was cooled to room temperature. Finally, the solid chromium complex (2) was washed thoroughly with water and followed by diethyl ether and dried at 50 °C. Other complexes (complexes 4 and 6) were prepared under the same method.

***Complex 1**: Light green, M.P.: 130 °C; Yield 88%: [Cr((Ligand 2: AA1H)(Ligand 1:BAH2)]Cl_3, Mol. Wt.: 797.49, Cr%: 6.52 (6.09); C%: 60.18 (60.00); H%: 4.64 (4.01); N%: 5.26 (4.99); Molar refraction: 1.436674 * 10^{-4}.*

***Complex 2**: Green, M.P.: 131 °C; Yield 89%: [Cr((Ligand 2: AA1)(Ligand 1:BAH)], Mol. Wt.: 688.99, Cr%: 7.54 (6.99); C%: 69.66 (68.01); H%: 5.08 (4.99); N%: 6.09 (5.86); Molar refraction: 1.436662 * 10^{-4}.*

***Complex 3**: Light green, M.P.: 134 ℃; Yield 86%: [Cr((Ligand 3: AAH2)(Ligand 1:BAH2)]Cl_3, Mol. Wt.: 916.49, Cr%: 5.67 (5.27); C%: 61.53 (60.91); H%: 4.58 (4.07); N%: 6.11 (5.81); Molar refraction: 1.436681* 10^{-4}.*

***Complex 4**: Green, M.P.: 128 ℃; Yield 89%: [Cr((Ligand 3: AAH)(Ligand 1:BAH)], Mol. Wt.: 807.99, Cr%: 6.43 (5.89); C%: 69.80 (68.98); H%: 4.95 (4.51); N%: 6.93 (6.59); Molar refraction: 1.436672* 10^{-4}.*

***Complex 5**: Green, M.P.: 137 ℃; Yield 87%: [Cr((Ligand 4: AnH)(Ligand 1:BAH2)]Cl_3, Mol. Wt.: 753.49, Cr%: 6.90 (6.27); C%: 62.11 (61.96); H%: 4.91 (4.78); N%: 5.57 (5.30); Molar refraction: 1.436660* 10^{-4}.*

***Complex 6**: Green, M.P.:135 ℃; Yield 88%: [Cr((Ligand 4: An)(Ligand 1:BAH)], Mol. Wt.: 644.99, Cr%: 8.06 (7.88); C%: 72.55 (71.60); H%: 5.42 (4.99); N%: 6.51 (6.07); Molar refraction: 1.436681* 10^{-4}.*

2.4. Synthesis of carbonyl compounds using prepared chromium complexes from benzyl bromide

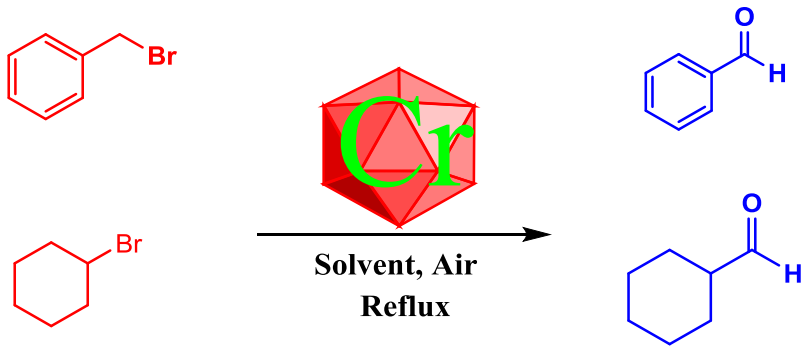
To show the applicability of the prepared catalysts (chromium complex), we aim to direct the synthesis of carbonyl compounds from benzyl bromide using prepared complexes under aerobic conditions in water. Therefore, in a 50 mL round bottom flask, 3 mmol of benzyl bromide, 5.0 mL of solvent, and 250 mg of the best-prepared chromium complex were stirred at 100 °C in water for an appropriate time. After the completion of the reaction, the reaction mixture was cooled to room temperature and 10 mL of ethyl acetate was added. Then, the obtained crude materials were injected into gas-chromatography tandem mass spectroscopy for the determination of yield and conversion of the reaction.

2.5. Antimicrobial assay of the chromium complexes

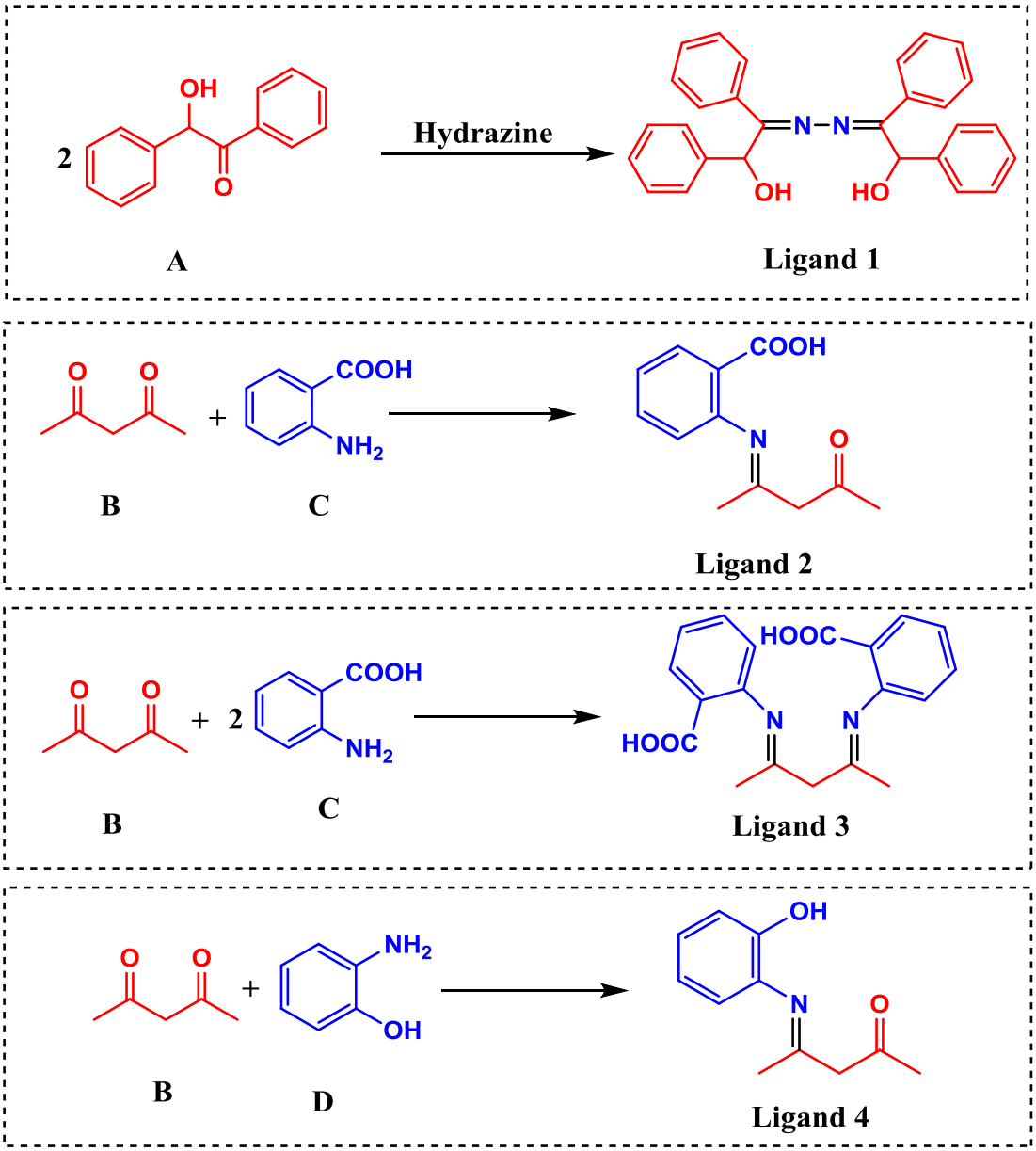
Five pathogenic microorganisms (*Staphylococcus aureus, pseudomonas aeruginosa, Proteus mirabilis* and *Escherichia coli*) have been selected to study the antibacterial activity of the ligands and their complexes. All the bacterial strains have been identified before use in Biology Department, Education for Pure Science College, Mosul University. The antibacterial activity has been evaluated by agar plate diffusion technique identifying a variety of medicinally important gram-positive and gram-negative. In this method, Nutrient agar plates have been seeded with 0.1 mL. of the broth culture of the tested microorganism containing (10^8) cells/ml., filter paper discs were impregnated with the tested materials then placed on the surface of seeded Nutrient agar plates, the plates were incubated at 37 °C for 24 h, the zone of inhibition have been measured for the determination of minimum inhibitory concentration (MIC), different concentrations of the tested materials (500, 250, 125 µg/ml) were used.

3. Results and Discussion

The importance of direct synthesis of carbonyl compounds from benzyl bromide in food chemistry, synthesis of drugs, antioxidants, and natural synthetic compounds has been recognized for several years. Due to the significance of the described compounds, our plan is to produce benzaldehyde derivatives from the oxidation reaction of benzyl bromide under the aerobic condition in water medium as a green solvent (**Scheme 2**). Four ligands were prepared as outlined in **Scheme 3** according to the previous reported literature [18, 19]. In this study, we prepared four different ligands including 2,2'-(hydrazine-1,2-diylidene)bis(1,2-diphenylethan-1-ol) (Benzoinazine-BAH2) (Ligand 1), (E)-2-((4-oxopentan-2 ylidene)amino)benzoic acid, (Acetylacetonemonoanthralidene-AA1H) (Ligand 2), 2,2'-(((2E,4E)-pentane-2,4-diylidene)bis(azaneylylidene))dibenzoic acid (Acetylacetonedianthralidene-AAH2) (Ligand3), and(E)-4-((2-hydroxyphenyl)imino)pentan-2-one(Acetylacetonemonohydroxyl anilidene AnH) (Ligand 4).



Scheme 2. Synthesis of benzaldehyde derivatives from benzyl/cycloalkyl bromide using chromium complex



Scheme 3. Synthetic routes for the preparation of four ligands.

After the preparation of four ligands, six types of chromium complexes were prepared as follows. Complex 1 was prepared through the treatment of 0.39 g of ligand 1 (BAH2) and 0.20 g of ligand 2 (AA1H) and 0.46 g of $CrCl_3.6H_2O$ under neutral conditions. In addition, complex 2 was prepared as the same amount of ligands 1 and 2 as well as the source of chromium reagent in the presence of 1.0 mL(dropwise) of sodium hydroxide 2.0 M. For the preparation of complex 3, the 0.39 g of ligand 1 (BAH2) and 0.32 g of ligand 3 (AAH2) as well as 0.46 g of $CrCl_3.6H_2O$ under neutral conditions were used. Notably, the basic complex 4 was provided as the same amount of ligands 1 and 3 as well as the source of chromium reagent in the presence of 1.0 mL of sodium hydroxide 2.0 M. Finally, for the preparation of complex 5, 0.39 g of ligand 1 (BAH2) and 0.16 g of ligand 4 (AnH), as well as 0.46 g of $CrCl_3.6H_2O$ was applied to afford corresponding complex 5 under neutral conditions. For the preparation of complex 6, the 1.0 of sodium hydroxide 2.0 was used to obtain complex 6. The chemical structure of the prepared complexes was shown in **Fig. 2**. The obtained chromium complexes were colored solids (light green or green), air-stable, insoluble in water and soluble in DMSO. The elemental analyses, metal contents and molecular weight revealed that the complexes had the formulas $[Cr(LH_X)(BAH_2)]Cl_3$ and $[Cr(LH_{X-1})(BAH)]$ in neutral (or slightly acidic) and basic medium, respectively.

The amount of the molar conductivities (93.00-94.01 & 8.03-13.01) $\Omega^{-1}cm^2mol^{-1}$ approached those expected for 1:3 and electrolytes (complexes 1, 3, and 5), for

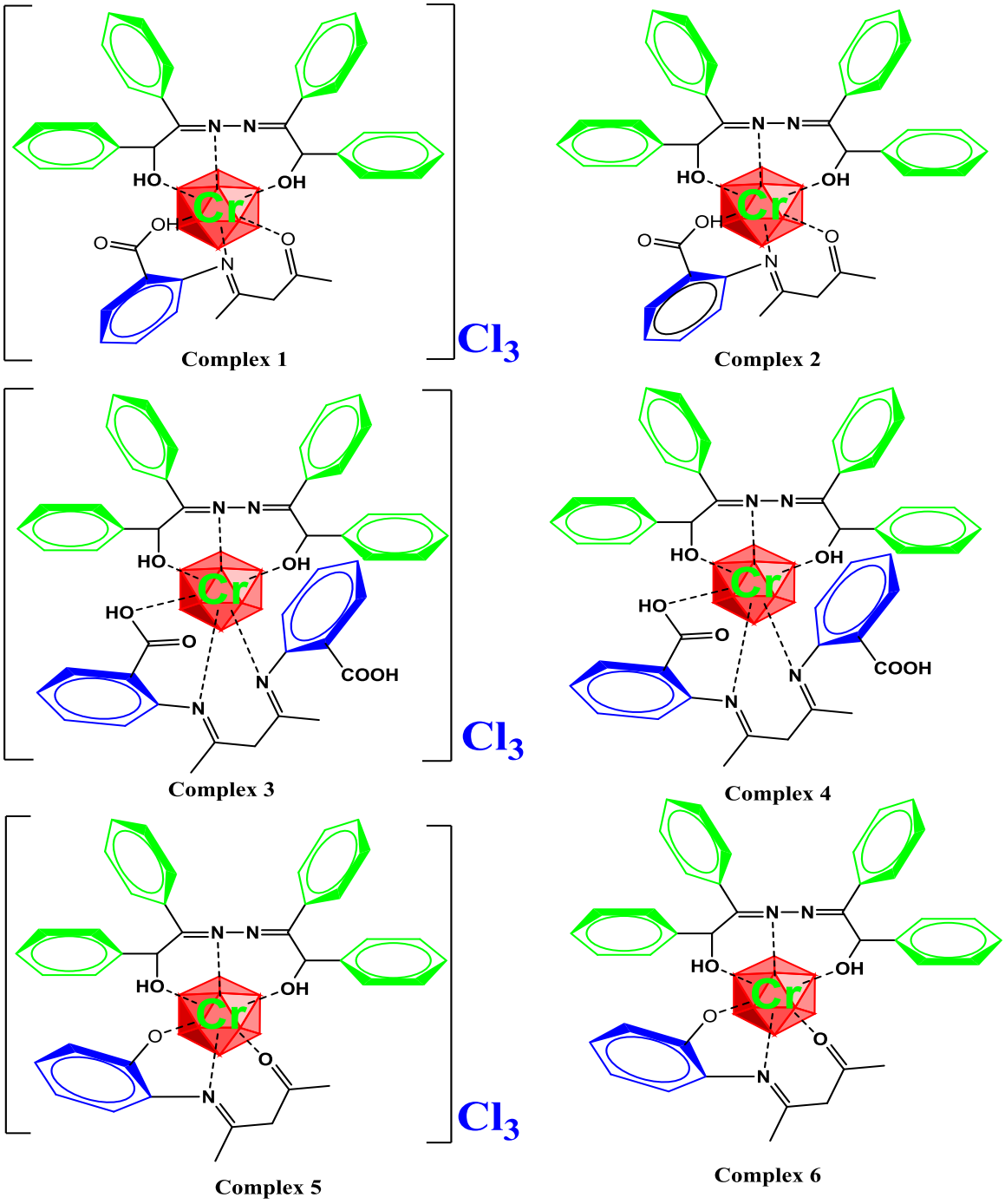


Fig. 2. The chemical structure of octahedral chromium complexes

complexes prepared in neutral (or slightly acidic) and non-electrolytes (complexes 2, 4, and 6), for complexes prepared in basic medium, respectively. At room temperature, the magnetic moments (3.72-3.89 B. M) indicated the presence of three unpaired electrons, chromium (III) complexes, assigned to a monomeric structure, having octahedral geometry. The refraction of the complexes in 10^{-3} M DMSO solution was in the range $1.436660x10^{-4}$-$1.436681x\ 10^{-4}$. The molar refraction is an additive and constitutive property. It has been used to construct the correct structure of the compound [20]. The magnetic moment in Bohr Magneto and molar conductance in Ω^{-1} cm^2 mol^{-1} was provided in **Table 1** for six chromium complexes.

After the successful preparation of the four ligands, the ligands were investigated using FT-IR spectroscopy (**Fig. 3**). The FT-IR spectrum of the ligands 3: AAH2, 2: AA1H and 4: AnH showed absorption bands at about 1575-1637 cm^{-1} due to the frequency of the group imine, and these bands shifted to lower frequencies when

forming the complex (**Fig. 4**). This indicates the consistency of the nitrogen atom with the metal ion in the neutral and basic medium determined at 422-428 cm^{-1}. The absorption bands appeared due to C=O and upon symmetry, they shifted towards lower frequencies as depicted in **Fig 4**. This indicates the consistency of the oxygen atom with the metal ion at 505-507 cm^{-1}, as well as absorption bands that return to OH groups at 3300-3402 cm^{-1} and the formation of complexes in the neutral or acidic shifted the frequency to a lower value. As for the blocked complexes in the basic medium, the bands of the OH group disappeared and new ones appeared, returning to C-O-C bonds.

Table 1. Some physical of the prepared complexes

No.	D×10^{-6} (c.g.s.u)	χ_g×10^{-6} (c.g.s.u)	χ_M×10^{-6} (c.g.s.u)	χ_A×10^{-6} (c.g.s.u)	μeff (B.M)	Λ_M	Mp °C	Color
Complex 1	298.02	7.55092	6021.78	6319.80	3.88	93.02	130	Light green
Complex 2	221.96	8.10358	5583.28	5805.24	3.72	13.01	131	Green
Complex 3	330.25	6.58971	6039.40	6369.68	3.89	93.00	134	Light green
Complex 4	254.22	7.00651	5661.19	5915.41	3.75	10.21	128	Green
Complex 5	282.82	8.00113	6028.77	6311.59	3.87	94.01	137	Green
Complex 6	206.76	9.00113	5805.63	6012.39	3.78	8.03	135	Green

μ_{eff} : Magnetic moment in Bohr Magneton, ^M = molar conductance in Ω^{-1} cm^2 mol^{-1}

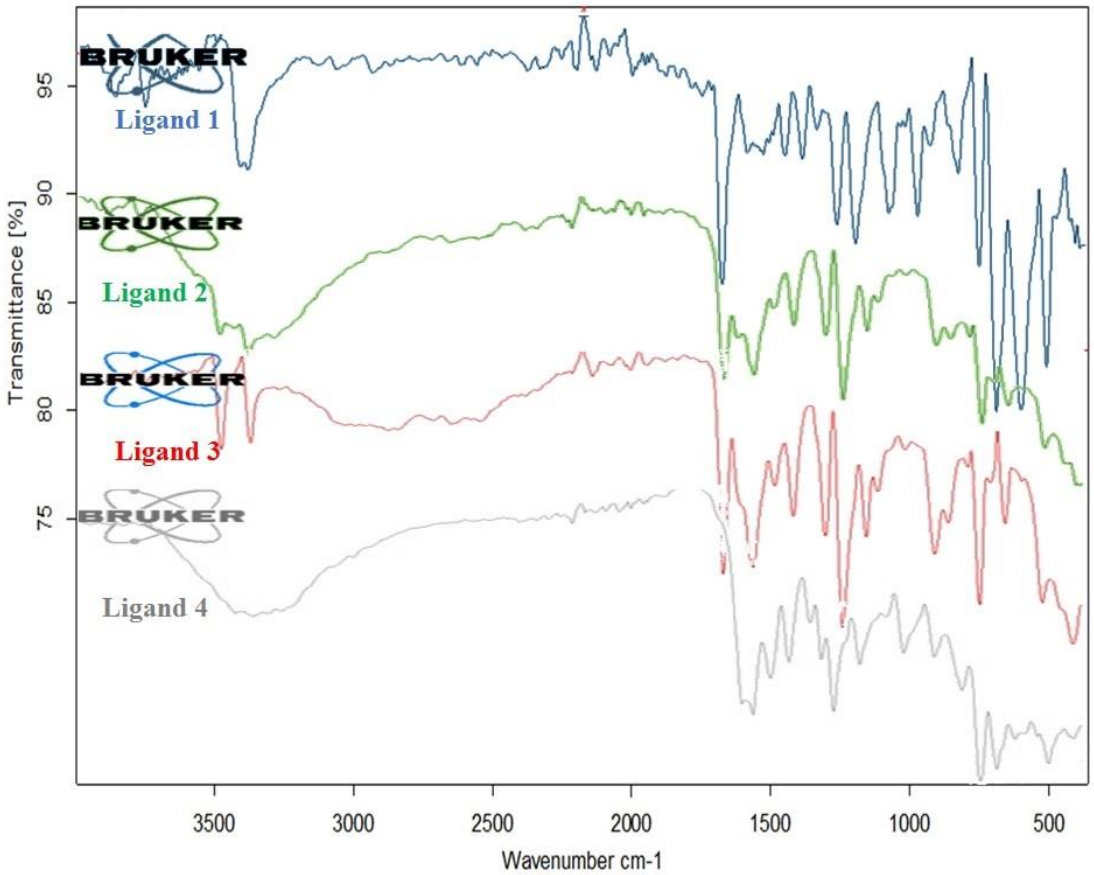


Fig. 3. FT. IR spectra of Ligand 1: BAH2; Ligand 2: AA1H; Ligand 3: AAH2; Ligand 4: AnH.

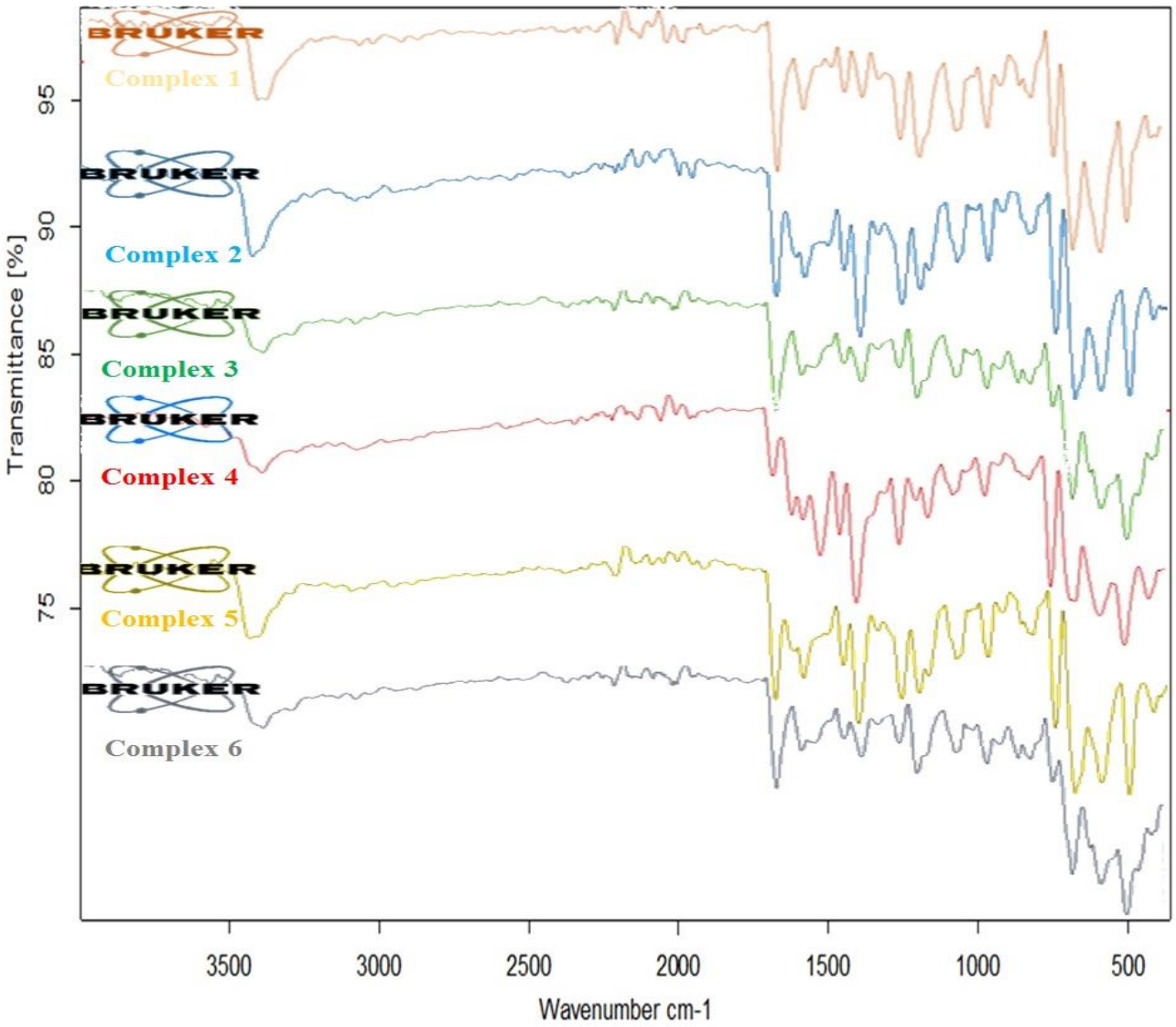


Fig. 4. FT-IR spectra: complex 1 (Ligand 1: Ligand 2- neutral condition); complex 2: (Ligand 1: Ligand 2-basic condition), complex 3: (Ligand 1: Ligand 3- neutral condition), complex 4: (Ligand 1: Ligand 3- basic condition), complex 5: (Ligand 1: Ligand 4- neutral condition), complex 5: (Ligand 1: Ligand 3- basic condition).

The UV-Vis of chromium complexes showed bands (υ_1, υ_2 and υ_3) at 10204-11764 cm^{-1},16447-17123 cm^{-1} and 20325-22738 cm^{-1} due to the transitions ^4A_2g (F)$\rightarrow$$^4T_2g$ (F), $^4A_2g(F)\rightarrow{}^4T_1g(F)$ and $^4A_2g(F)\rightarrow{}^3T_1g(P)$, respectively [18, 19]. However, the electronic spectral data suggested octahedral geometry for all the complexes [21-24] (**Table 2**).

The prepared chromium complexes provide an ideal model for studying catalytic organic reactions under aerobic oxidation conditions. As mentioned above, we would like to investigate the catalytic activity of synthesized chromium complexes as efficient catalysts in the direct synthesis of carbonyl compounds from benzyl bromide under aerobic conditions. After the preparation and characterization of chromium complexes, the catalytic systems were used in the synthesis of benzaldehyde derivatives. Therefore, to optimize the reaction conditions, we used benzyl bromide as a starting material to synthesize benzaldehyde as a model reaction under thermal conditions. The optimized results are shown in **Table 3**.

As shown in **Table 3** (entries 1-4), in the presence of various solvents including ethanol, methanol, THF, and water, the model reaction was performed using 200 mg of complex 1. The final product was obtained in 11%, 19%, 32%, and 63% for ethanol, methanol, THF, and water, respectively. By changing the amount of catalytic system from 200 mg to 250 mg of complex 1, the 250 mg of complex 1 was the best amount of the pointed

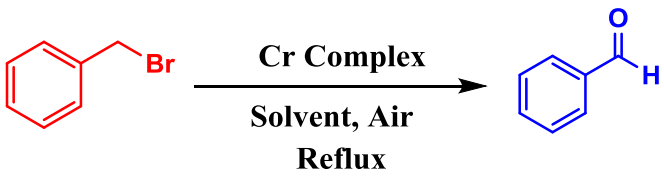
complex (entries 4-7). In addition, different types of neutral chromium complexes including complexes 1, 3, and 5 were checked. Complex 5 shows the best result among complexes 1, 3, and 5 (entries 7-9). Also, the model reaction was performed using basic complexes and the results were 90%, 89%, and, 92% for complexes 2, 4, and, 6, respectively. In the absence of the chromium complexes, the oxidation of bezyl bromide was observed at least yield (entry 13).

Up to now, there is no report in the literature on the application of chromium complexes for the direct synthesis of carbonyl compounds using benzyl halide. With the optimal conditions in hand, the oxidation of

Table 2. The electronic spectra of chromium (III) complexes

No.	$^4A_2g(F)\rightarrow{}^4T_2g(F)$ ν_1 (cm^{-1})	$^4A_2g(F)\rightarrow{}^4T_1g(F)$ ν_2 (cm^{-1})	$^4A_2g(F)\rightarrow{}^3T_1g(P)$ ν_3 (cm^{-1})	C.T (cm^{-1})
1	10204	16667	20762	35714
2	11010	16779	22738	35635
3	11015	16722	20255	35714
4	11062	17123	22243	34247
5	11764	16722	21738	36496
6	11020	16447	20325	34482

Table 3. Optimization of the reaction conditions for the model reaction[a].

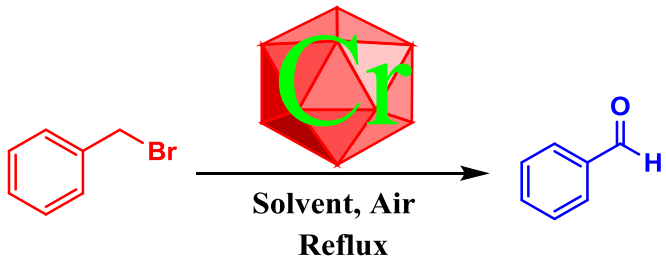


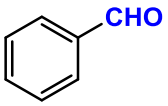
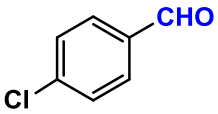
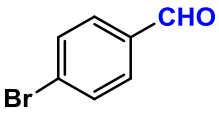
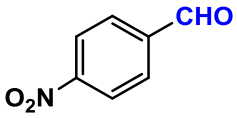
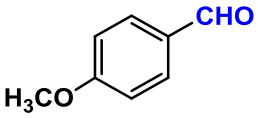
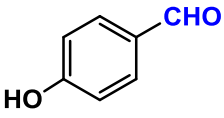
Entry	Type of Complex	(mg)	Solvent	T (°C)	Yield (%)	Time (h)
Neutral Complexes						
1	Complex 1	200	EtOH	Reflux	11%	5
2	Complex 1	200	MeOH	Reflux	19%	5
3	Complex 1	200	THF	Reflux	32%	5
4	Complex 1	200	H_2O	Reflux	63%	5
5	Complex 1	230	H_2O	Reflux	75%	5
6	Complex 1	250	H_2O	Reflux	91%	5
7	Complex 1	270	H_2O	Reflux	90%	5
8	Complex 3	250	H_2O	Reflux	92%	5
9	Complex 5	250	H_2O	Reflux	94%	5
Basic Complexes						
10	Complex 2	250	H_2O	Reflux	90%	5
11	Complex 4	250	H_2O	Reflux	89%	5
12	Complex 6	250	H_2O	Reflux	92%	5
13	No Catalyst	-	H_2O	Reflux	< 5.0%	12
14	$CrCl_3.6H_2O$	340	H_2O	Reflux	< 56.0%	12

a)Benzyl bromide (3.0 mmol), Solvent: 5.0 mL, b) GC Yields.

different substituted benzyl bromide derivatives was tested to check the scope of the benzyl bromide derivatives and the efficiency of chromium complexes. (**Table 4**). In this study, various benzyl bromide derivatives were selected with both electron-donating groups and electron withdrawing groups at *–ortho*, -*meta*, and *–para* positions. Under the optimum conditions, the corresponding benzaldehyde derivatives were obtained in moderate to excellent yields.

Table 4. Synthesis of benzaldehyde derivatives using six types of chromium complexes under aerobic oxidation [a]



					
Complex 1:	Complex 2:	Complex 1:	Complex 2:	Complex 1:	Complex 2:
91%,[b] 4.3 h	90%, 4.1 h	90%, 3.9 h	93%, 3.6 h	97%, 2.9 h	96%, 2.9 h
Complex 3:	Complex 4:	Complex 3:	Complex 4:	Complex 3:	Complex 4:
92%, 4.6 h	89%, 4.4 h	91%, 3.5 h	92%, 3.5 h	97%, 2.9 h	96%, 3.0 h
Complex 5:	Complex 6:	Complex 5:	Complex 6:	Complex 5:	Complex 6:
94%, 4.0 h	92%, 4.0 h	91%, 3.0 h	93%, 2.9 h	97%, 2.5 h	94%, 2.3 h
					
Complex 1:	Complex 2:	Complex 1:	Complex 2:	Complex 1:	Complex 2:
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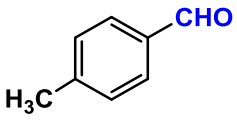
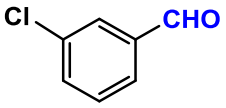
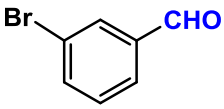
Complex 3:	Complex 4:	Complex 3:	Complex 4:	Complex 3:	Complex 4:
93%, 3.0 h	93%, 2.7 h	89%, 3.2 h	90%, 3.6 h	83%, 4.0 h	83%, 3.8 h
Complex 5:	Complex 6:	Complex 5:	Complex 6:	Complex 5:	Complex 6:
92%, 2.7 h	96%, 2.6 h	92%, 2.9 h	96%, 2.9 h	86%, 3.7 h	88%, 3.5 h
					
Complex 1:	Complex 2:	Complex 1:	Complex 2:	Complex 1:	Complex 2:
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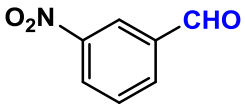
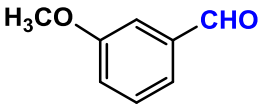
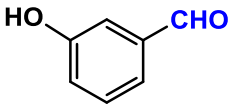
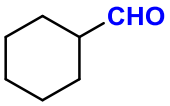
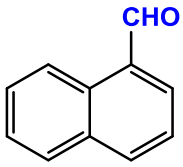
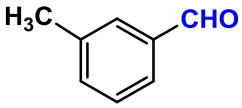
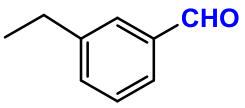
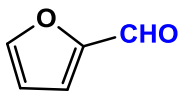
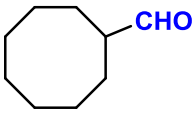
Complex 3:	Complex 4:	Complex 3:	Complex 4:	Complex 3:	Complex 4:
93%, 4.0 h	91%, 3.7 h	88%, 2.9 h	89%, 3.3 h	95%, 2.9 h	94%, 2.8 h
Complex 5:	Complex 6:	Complex 5:	Complex 6:	Complex 5:	Complex 6:
92%, 3.6 h	93%, 2.9 h	80%, 3.0 h	81%, 3.2 h	93%, 2.8 h	96%, 2.2 h

					
Complex 1:	Complex 2:	Complex 1:	Complex 2:	Complex 1:	Complex 2:
97%, 3.4 h	97%, 3.5 h	92%, 4.0 h	89%, 3.8 h	83%, 4.8 h	81%, 6.1 h
Complex 3:	Complex 4:	Complex 3:	Complex 4:	Complex 3:	Complex 4:
99%, 2.3 h	99%, 2.2 h	91%, 3.8 h	92%, 3.0 h	87%, 4.5 h	83%, 6.8 h
Complex 5:	Complex 6:	Complex 5:	Complex 6:	Complex 5:	Complex 6:
99%, 2.0 h	96%, 2.0 h	90%, 3.6 h	94%, 2.9 h	89%, 5.0	86%, 5.0 h
					
Complex 1: 82%, 5.0 h	Complex 2: 83%, 4.8 h	Complex 1: 76%, 7.2 h	Complex 2: 77%, 7.0 h	Complex 1: 89%, 5.0 h	Complex 2: 88%, 4.8 h
Complex 3:	Complex 4:	Complex 3:	Complex 4:	Complex 3:	Complex 4:
86%, 4.7 h	83%, 4.5 h	77%, 5.6 h	80%, 5.5 h	90%, 3.9 h	90%, 3.7 h
Complex 5:	Complex 6:	Complex 5:	Complex 6:	Complex 5:	Complex 6:
85%, 5.0 h	86%, 5.2 h	79%, 3.9 h	77%, 3.8 h	91%, 3.1 h	89%, 3.5 h
					
Complex 1:	Complex 2:	Complex 1:	Complex 2:	Complex 1:	Complex 2:
89%, 4.0 h	90%, 4.1 h	71%, 4.0 h	69%, 5.0 h	63%, 7.0 h	65%, 7.0 h
Complex 3:	Complex 4:	Complex 3:	Complex 4:	Complex 3:	Complex 4:
92%, 3.6 h	95%, 4.0 h	67%, 5.0 h	66%, 5.5 h	65%, 6.9 h	68%, 6.9 h
Complex 5:	Complex 6:	Complex 5:	Complex 6:	Complex 5:	Complex 6:
90%, 2.8 h	96%, 3.9 h	65%, 5.0 h	67%, 6.0 h	69%, 7.0 h	67%, 6.8 h

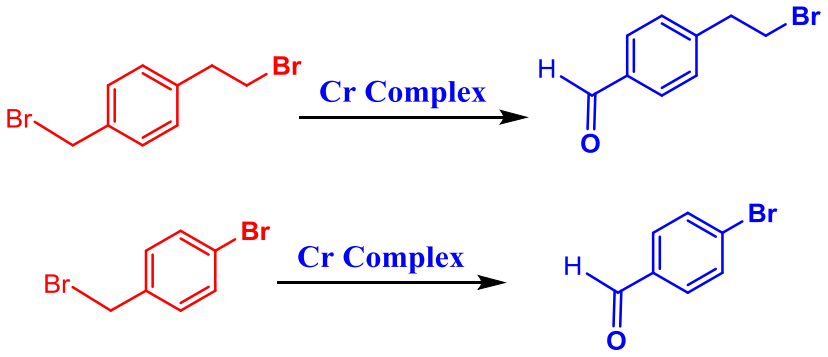
a) Reaction conditions: Benzyl bromide (3.0 mmol), H_2O: 5.0 mL, Catalyst: 250 mg, b) GC Yield.

To show the efficiency of selectivity of the prepared complexes, we used 1-(2-bromoethyl)-4-(bromomethyl)benzene and 1-bromo-4-(bromomethyl)benzene as specific substrates for evaluation of the selectivity of prepared chromium complexes. Our results show that all of the chromium complexes were selective towards benzylic oxidation versus alkyl oxidation as well as benzylic oxidation versus arene oxidation (**Scheme 4**).

In this part, to show the advantage and efficiency of the presented method in the oxidation of benzyl bromide derivatives to carbonyl compounds, we have compared our results with other reported catalysts. As observed in **Table 5**, the current study is worthwhile in yield, time, catalytic loading, and less byproduct.

In the present study, all of the synthesized chromium complexes were monitored in-vitro for their biological activity. Many chemical compounds had a good ability to attack the bacteria through their effects on the synthesis of ribonucleic acid which could be resulted from the inhibition action of these compounds on the DNA of the bacteria which caused inhibition of the activities of DNA gyrase enzyme including the separation of supercoiling or decant enation or

unknotting of the DNA. Moreover, the antibacterial agent was known to attack the cell in a variety of ways such as killing or inhibiting the growth of microorganisms by affecting special target sites like the synthesis of cell wall, protein and nucleic acid or by inhibiting the function of the cell membrane, binding of the sulfhydryl groups of the cell enzymes with the complexes. Numerous experiments have been done to determine the antimicrobial influence of the complexes. All the ligands and compounds have been screened for antibacterial activity in vitro against *Staphylococcus aureus, pseudomonas aeruginosa, Proteus mirabilis* and *Escherichia coli*. No effects have been observed.



Scheme 4. Investigation of selectivity of prepared complexes

Table 5. Comparison of reported catalysts in this work for oxidation of benzyl bromide to benzaldehyde

Entry	Catalyst	Solvent	T (°C)	Time	Condition	Yield (%)	Ref.
1	4-hydroxypyridinium nitrate@SiO_2	H_2O	20	0.05 h	MW	99%	[2]
2	2,2,6,6-Tetramethyl-1-piperidinyloxy free radical, Potassium Nitrite	H_2O	Reflux	3.5 h	Heating	95%	[3]
3	4-methylmorpholine N-oxide; 1-ethyl-3-methyl-1H-imidazol-3-ium chloride	Ionic Liquid	100	0.03 h	MW	95%	[4]
4	bis-{4-methoxy-phenyl}-selenoxyde; sodium hydrogencarbonate	THF, Acetonitrile	75	10 h	Heating	93%	[25]
5	$(NH_4)_4[ZnMo_6O_{18}(OH)_6]$	H_2O, CH_3CN	60	12 h	Heating	88%	[26]
6	manganese(IV) oxide	Chloroform	60	2 h	Heating	80%	[27]
7	4-methylmorpholine N-oxide	Solvent-free	80	0.5 h	Ultrasound	82%	[28]
8	Complex 5	H_2O	Reflux	4 h	Heating	94%	This work

4. Conclusions

In conclusions, we have synthesized four types of ligands including 2,2'-(hydrazine-1,2-diylidene)bis(1,2-diphenylethan-1-ol) (Benzoinazine-BAH2) (Ligand 1), (E)-2-((4-oxopentan-2 ylidene)amino)benzoic acid, (Acetylacetonemonoanthralidene-AA1H) (Ligand 2), 2,2'-(((2E,4E)-pentane-2,4-diylidene)bis(azaneylylidene))dibenzoic acid (Acetylacetonedianthralidene-AAH2) (Ligand 3), and (E)-4-((2-hydroxyphenyl)imino)pentan-2-one (Acetylacetonemonohhydroxyanilidene-AnH) (Ligand 4). The prepared ligands were characterized using FT-IR, ^{1}H NMR and elemental analysis. Then, the prepared ligands contributed to the preparation of six types of chromium complexes as shown above. The prepared chromium complexes were analyzed using FT-IR, UV-Vis, elemental analysis, magnetic moment and molar conductivities. The six types of chromium complexes were employed for the direct synthesis of benzaldehyde derivatives from benzyl bromide. In addition, the biological activity of prepared chromium complexes was investigated. Our results show that the prepared catalysts were efficient catalysts for the versatile oxidation of benzyl bromide derivatives. Also, to investigate the selectivity of the prepared chromium complexes, we used two specific substrates. Our results show that the prepared catalysts were selective and efficient in this reaction.

Acknowledgements

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