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# The use of a new Co(II) complex as a catalyst in catalytic reduction process

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**Abstract**
*The aim of this work was to evaluate the performance of new Co(II) complex as a catalystin catalytic reduction processusing 4-nitroaniline as model compound. For this purpose,a new Co(II) complex was synthesized and several approaches to the elucidation of its structure such as the elemental analysis, molar conductivity measurement FT-IR, the UV–Vis spectrophotometry, magnetic susceptibility measurement, and thermal gravimetric analysis were applied. This complex was found to bean efficient catalyst for catalytic reduction of p-nitroaniline.The Catalytic reduction result shows fast reduction in presence of Co(II) complex (70.6%) after 15 min.*

***Keywords:****Co(II)complex; Spectrophotometry; TG/DTGand catalytic study*



## 1. Introduction

Nitroarenes are a widely organic pollutant in waste water. Thus, the removal of nitroarenes is evermore an important issue. Various processes have been developed, including adsorption, photocatalysis, electrochemical treatment,the electro-Fenton method, electrocoagulation, catalytic hydrogenation, etc. Also, nitroaniline derivatives have been used as a precursor in the chemical synthesis of azo dyes, antioxidant compounds, poultry medicine, antiseptic agents, etc. However, avoiding the use of organic solvents, the improvement of suitable processes for removing nitroarenes in aqueous media under mild conditions is still needed [1-4]. The reduction of p-nitroaniline to p-phenylenediamine is a valuable and important chemical reaction. Especially, p-phenylenediamine is widely used to prepare of industrial chemicals such as thermoplastics, textile fibers, conducting polymers, and rubber antioxidants. Various metals and metal oxide nanoparticle composites have been used for the reduction of p-nitroaniline [5-8]. The catalytic reactivity of the synthesized compounds powder was tested for the reduction of 4-nitroaniline to 4-aminoaniline using $NaBH_4$ as the reducing agent at room temperature. This reaction has also been used earlier to examine the catalytic activity of different synthesized compounds.

## *2.* Experimental section

### 2.1. Chemicals used

All used materials were bought from Fluka, Prolabo and Sigma Aldrich Companies and are used without further purification.

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### 2.2. Apparatus

Elemental analyses (Elemen. Analy. -Vario EL Fab. CHNS Nr.- 11042023) was used to determine the content of carbon, hydrogen, and nitrogen, Infrared spectra were recorded as KBr disc use a FTIR-IR prestige 21 covering the frequency range 400-4000 $cm^{-1}$. Perkin Elmer analyzer equipment's-Shimadzu was used for thermal study from 50 to 1000 $^{O}C$ under a nitrogen air flow of 50 mL $min^{-1}$ and a heating rate of 10 $^{O}C$ $min^{-1}$. Melting point measurements were recorded using GALLENKAMP melting point apparatus.Molar conductance measurement ($1x10^{-3}$ M in DMF solvent) was measured at ambient temperature by JENWAY 3450 pH & Conductivity meter (JCM-3450).

### 2.3. Synthesis of the catalyst

The metal salt selected for the synthesis of metal complex under study is cobalt chloride hexahydrate ($CoCl_2.6H_2O$). A general procedure was followed for the preparation of thecomplex as: An equimolar ratio of an aqueous solution of cobalt chloride was added dropwise to an ethnolic solution of HL under stirring at room temperature (ligand: metal) (1:2). After complete addition, the reaction mixture was refluxed for 4h with constant stirring on a water bath whereupon the complex precipitated. The precipitated solid was filtered, washed several times by ethyl alcohol then diethyl ether and finally dried in vacuum desiccators over anhydrous $CaCl_2$.

### 2.4. Catalytic activity test

In a typical experiment, 25 ml of 0.05 M $NaBH_4$ aqueous solution was mixed with 1 ml of 1 mM 4-nitroaniline aqueous solution and catalyst (0.01gm) in around bottom flask. To study the trend of reduction of nitro groups,3 mL of this suspension was sampled at different time intervals and after removal of the catalyst, was monitored using UV–Vis spectrophotometer [9,10].

## 3. Results and discussion

The synthesis of the new Co(II) complex was carried outusing a common procedureby the reaction of a stoichiometricamount of the ligand, L with the selected metal ion. The analytical data of Co(II) complex reveal that thereactions between metal ion and the ligand are performedin 2:1 (M:L) molar ratio. Some physical properties and analytical data of the complex were summarized in Table 1.

**Table 1:** Analytical data and some physical properties of Co(II) complex

| compound | Color (% yield) | M.P (ºC) | Elemental analysis, Found / (Calcd.) % | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | **S** | Cl | M |
| Co(II) complex | Rose (75.8) | >360 | 38.35 (38.06) | 2.75 (2.64) | 7.55 (7.72) | 4.75 (4.41) | 14.76 (14.65) | 15.90 (16.24) |

### 3.1. Molar conductance measurements

The molar conductivity measurement for $1\times10^{-2}$ M ofCo(II) complex in DMSO at room temperature, 11.62 $\Omega^{-1}mol^{-1}cm^{2}$,indicates that thiscomplex is non-electrolytes[11].

### 3.2. Infrared spectra investigation

The IR spectra ofCo(II) complex show a shift of the υ(C=N) to lower frequencycompared with the free ligand band at 1620 $cm^{-1}$. This shift indicates coordination of the azomethinegroup to the metal ions [12]. The υ(C=O) is shifted to lower wave numbers in Co(II) complex suggests the weakening of (C=O) and formation of stronger (M-O) bond as a result of the coordination of carbonyl oxygen to the metal ions [13]. The appearance of non-ligand bands of medium intensity at 548 $cm^{-1}$ in assigned to υ(M–N) strengthened the linkage of metal and nitrogen of azomethine group and bands of medium intensity at 602 $cm^{-1}$ is attributed to υ(M–O) [14].

### 3.3. Electronic spectraand magnetic behavior of the metal complex

Appearance ofonemain absorption band in the electronic spectra of Co (II) complex at 530 nm assigned to the transition $^4A_2(F) \rightarrow {}^4T_1(P)$ suggesting tetrahedral geometry about the Co (II) complex. Additionally, the value of the molar magnetic susceptibility measured at room temperature confirm the tetrahedral geometryof Co (II) complex[15,16].

### 3.4. Thermal study (TG/DTG) study

From TG / DTGthermogram Fig.1, the mass loss was calculatedfor the different steps of decomposition process and compared with those theoretically calculatedfor the suggested formulae. Co(II) complex have hydrated water molecules where they are start to decompose at 35 $^{O}$C. The decomposition process for Co(II) complex includes complete degradation and evaporation of organic ligand through four steps and the end product of decomposition process is carbon and metallic residue.

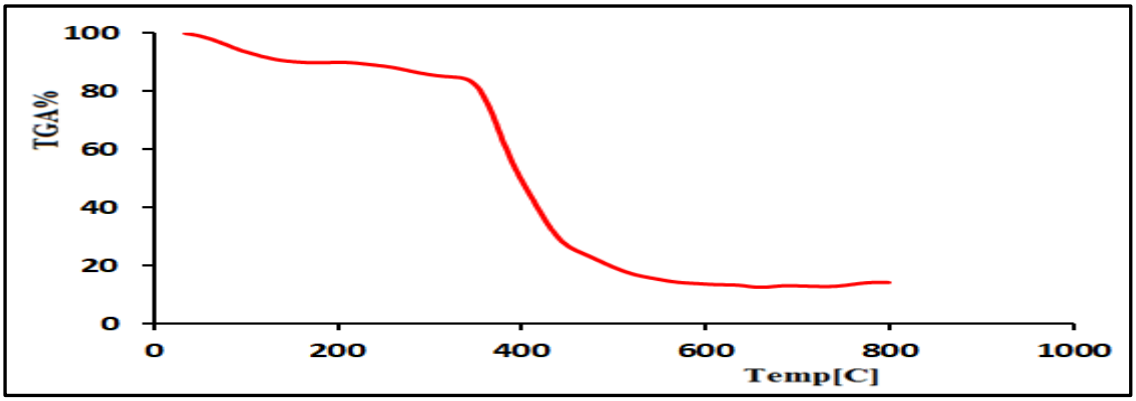


**Figure 2:**TG-thermograme of Co(II) complex

### 3.5. Catalytic reduction of 4-nitroaniline

The catalytic activities of synthesized compound for the 4- nitroaniline reduction was observed by monitoring the color change of 4-nitroaniline from yellow to faded, and monitored the decrease of absorbance at 300-500 nm. Presence of the p-PDA can further be confirmed with the appearance of the peak near 305 nm [17]. The reduction of 4-nitroaniline to 4-phenylenediamine without catalyst is quite slow, wearers in presence of catalyst the reduction percent was found to be 70.6%.The percent reduction as a function of time in the presence of Co(II)complex is shown in Fig2.

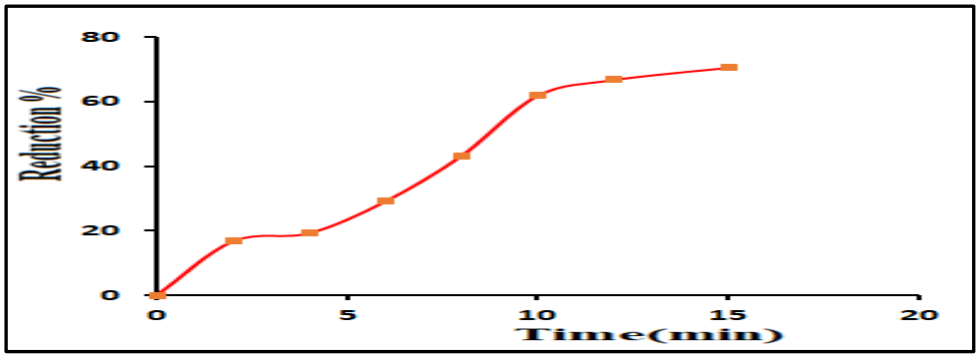


**Figure 2**: Time required for treduction of 4-NA in presence of Co(II) complex.

Conclusion

In conclusion, Co(II) complex was designed and synthesized to apply as a catalyst for reduction of 4-nitroaniline into 4-aminoaniline. This complex showed a results make it a suitable for environmental applications.

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**Conflicts of interest**

The author declares no conflict of interest.

***References***

1. *S. Dayan, S. Öztürk, N.Kayaci, N. K. Ozpozan and E. Öztürk, Fabrication of MgAl2Si2O8: M0.01 (M =Ni2+, Cu2+, Pd2+, Pt2+ and Ru3+): catalytic effects for the reduction of 2- or 4-nitroanilines in waterj. Bull. Mater. Sci. 38, 1651–1663, 2015,*
2. *J. W. Ko, S. Jeon&W.BaeKo,Catalytic activity of nickel(II) oxide nanoparticle-[C60]fullerene nanowhisker composite for reduction of 4-nitroaniline j. Fullerenes, nanotubes and carbon nanostructures, VOL. 28, 642–649, 2020.*
3. *Y. Yulizar, D. Apriandanu, Z.Zahra, SiO2/NiFe2O4 nanocomposites: Synthesis, characterization and their catalytic activity for 4-nitroaniline reduction j. Materials Chemistry and Physics 261, 124243, (2021).*
4. *R. Begum, G. Ahmad, J. Najeeb, W.Wu, A. Irfan, M.Azam, Ja. Nisar, Z. H. Farooq, Stabilization of silver nanoparticles in crosslinked polymer colloids through chelation for catalytic degradation of p-nitroaniline in aqueous medium j. Chemical Physics Letters 763, 138263, (2021).*
5. *A. M. Signori, K.O. Santos, R.Eising,B. L. Albuquerque,F. C. Giacomelli, and J. B. Domingos,Formation of Catalytic Silver Nanoparticles Supported on Branched Polyethyleneimine Derivatives j. Langmuir 26(22), 17772–17779, 2010.*
6. *E. M. Bakhsh , F. Ali, S. B. Khan, H. Marwani, E. Y. Danish, A. M. Asiri, Copper nanoparticles embedded chitosan for efficient detection and reduction of nitroaniline, International Journal of Biological Macromolecules 131, 666–675 (2019).*
7. *Z.H. Farooqi, A. Masaud, R. Begum, A. Irfan, Physicochemical aspects of reduction of 3-Nitroaniline using methacrylamide based nano-hybrid catalyst, Chemical Physics Letters 759, 137992 (2020).*
8. *I. Sargin, Efficiency of Ag(0)@chitosan gel beads in catalytic reduction of nitroaromatic compounds by sodium borohydride, International Journal of Biological Macromolecules 137, 576–582 (2019).*
9. *Z. Liu, J. Du, X. Jin, P. Li, X.Jiang, J. Yuan, Polyurethane/Keratin/AgNPsnanofibrous mats as catalyst support for 4-nitroaniline reductionJ. Materials Letters 237, 9–13 (2019).*
10. *P. Das, S. Ghosh, M.Baskey, Heterogeneous catalytic reduction of 4-nitroaniline by RGO-Ni-nanocomposite for water resource managementJ. Journal of Materials Science: Materials in Electronics, 30:19731–19737 (2019).*
11. *Y. Liu, L. Yang, D. Yin, Y. Dang, L.Yang, Q. Zou, J. Li, J. Sun, Solvent-free synthesis, characterization, biological activity of Schiff bases and their metal (II) complexes derived from ferrocenylchalcone, Journal of Organometallic Chemistry 899, 120903 (2019).*
12. *D.M. Aziz, H. J.Azeez,Synthesis of new ß-lactam- N-(thiazol-2-yl)benzene sulfonamide hybrids: Their in vitro antimicrobial and in silico molecular docking studies, Journal of Molecular Structure 1222, 128904 (2020).*
13. *A. A. Alothman, Z. M. Almarhoon, Nano-sized some transition metal complexes of Schiff base ligand based on 1-aminoquinolin-2(1H)-one, Journal of Molecular Structure 1206, 127704 (2020).*
14. *I. Althagafi1, M. G. Elghalban, N.M. El-Metwaly, Novel Synthesized BenzesulfonamideNanosizedComplexes;Spectral Characterization, Molecular Docking, Molecular Modeling and Analytical Application J. Journal of Inorganic and Organometallic Polymers and Materials, 29:876–892 (2019).*
15. *M. S. Refat, H. M. A. Killa and H. Fetooh, Spectroscopic and thermal characterization of Cu(II), Co(II), Ni(II) and Mn(II)complexes of fluorescent dye 4-N,N-dimethyl-ethanol amine-N-allyl-1,8-naphthalimide (4DMEAN), J. Mol. Struct. 983, 122–132 (2010).*

***16.*** *S. S. Kandil. G. Y. Ali and A. El-Dissouky, Cobalt(II, III) and copper(II) complexes of 3-(2-furylidene) hydrazino-5,6-diphenyl-1,2,4-triazine, Transition Metal Chem. 27: 398–406, (2002).*

***17.*** *M. Kr. Mahto, D. Samanta, S. Konar, H. Kalita, and A. Pathaka,N, S doped carbon dots—Plasmonic Au nanocomposites for visiblelightphotocatalytic reduction of nitroaromatics j. J. Mater. Res., Vol. 33, No. 23, Dec 14, 2018.*

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