ISSN: 2349 - 4891
International
Journal of Recent Research and Applied Studies
(Multidisciplinary Open Access Refereed e-Journal)

A colorimetric new synthesized sensor Co(II) complex for pollution detection

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Received 6th April 2021, Accepted 15th April 2021

Abstract
Throughout this study, a new synthesized Co(II) complex was characterized by fully physicochemical and spectroscopic methods such as the elemental analysis, FT-IR, the UV–Vis spectrophotometry, and thermal gravimetric analysis. This complex was found to be an efficient chemosensor able to detect the organic pollutants and so can be removed it. The organic pollutants such as 4-nitrophenol can be detected and treated through the reduction process in which 4-nitrophenol reduced to 4-aminophenol in presence of sodium borohydride as the reducing agent at room temperature.

Keywords: *Colorimetric sensor; Metal complex; Spectrophotometry; 4-nitro phenol; 4-amino phenol.*

1. Introduction

The huge number of by-products released form herbicide, insecticide and synthetic dye manufacturing industries are the main sources of pollutants such as nitrophenol and its derivatives. These nitrophenol compounds are stable in environment and also exhibit high-degree of toxicity and sustained impact on humans, animals and plants. The 4-nitrophenol is considered as hazardous waste and priority toxic pollutants by US Environmental Protection Agency, as it causes severe damage to central nervous system (CNS), liver, kidney and human blood [1,2]. Thus, their total quantity should be reduced or changed to another less toxic and useful chemical. 4-nitrophenol (4-NP) is one of the major class of environmental pollutants, while 4-aminophenol (4-AP) is a useful raw material in several industries including pesticides, dyes and cosmetic products. Consequently, researchers have developed various methods such as electrolytic reduction, metal-acid reduction, and catalytic hydrogenation to convert 4-NP to 4-AP. Amongst them, catalytic hydrogenation has proven to be an effective method, it has a high conversion rate, almost no effect on the environment and with no acid waste production [3].

Catalytic reduction of 4-NP has advantages of being more effective, highly selective and taking place under mild conditions. Additionally, and more importantly, the sole product from the catalytic reduction of 4-NP, 4-aminophenol (4-AP), is less toxic and of great commercial value, yielding benefits in the photographic, pharmaceutical, agrochemical and textile industries. Catalytic reduction, therefore, serves as an eco-friendlier route to removing the negative effect of NP on the environment. As a result, there exists an unrelenting urge to develop useful catalysts for the efficient conversion of these toxic NP compounds to the less toxic amino phenols [4].

The catalytic reactivity of the synthesized compounds powder was tested for the reduction of 4-nitrophenol to 4-aminophenol 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.

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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.

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 cobalt complex by general method

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 the complexes 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 complexes 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

About 1 mL aqueous solution of 4-nitrophenol (1mmol) and 10 mL of freshly prepared aqueous solution of $NaBH_4$ (50 mmol) were taken in a 250 mL beaker. To the above mixture 0.01gm of the catalyst was added with constant stirring at room temperature. The decolorization of the mixture indicated the complete reduction of 4-nitrophenol (yellow colored solution) to 4-aminophenol and the time taken was noted, fig 2 [5].

3. Results and discussion

The synthesis of the new Co(II) complex was carried out using a common procedure by the reaction of a stoichiometric amount of the ligand, HL with the selected metal ions. The analytical data of Co(II) complex reveal that the reactions between metal ion and the ligand are performed in 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 1×10^{-2} M of Co(II) complex in DMSO at room temperature, 11.62 $\Omega^{-1}mol^{-1}cm^2$, indicates that this complex is non-electrolytes [6].

3.2. Infrared spectra investigation

The IR spectra of Co(II) complex show a shift of the υ(C=N) to lower frequency compared with the free ligand band at 1620 cm^{-1}. This shift indicates coordination of the azomethine group to the metal ions [7]. 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 [8]. 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) [9].

3.3. Magnetic behavior of the metal complexes and Electronic spectra

The molar magnetic susceptibility values for powder sample of the Co(II) complex was measured at room temperature and used to calculate the corrected magnetic moments. Co(II) complex was found to be paramagnetic and their observed magnetic moments values are 5.39 BM indicating presence of three unpaired electrons. The electronic spectra of Co (II) complex showed one main absorption band at 530 nm assigned to the transition $^4A_2(F) \rightarrow {}^4T_1(P)$ suggesting tetrahedral geometry [10,11].

3.4. Thermogravimetric analysis (TG/DTG) study

From TG / DTG thermogram Fig.1., the mass loss was calculated for the different steps of decomposition process and compared with those theoretically calculated for the suggested formulae. Co(II) complex have hydrated water molecules where they are start to decompose at 35 ^OC. 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.

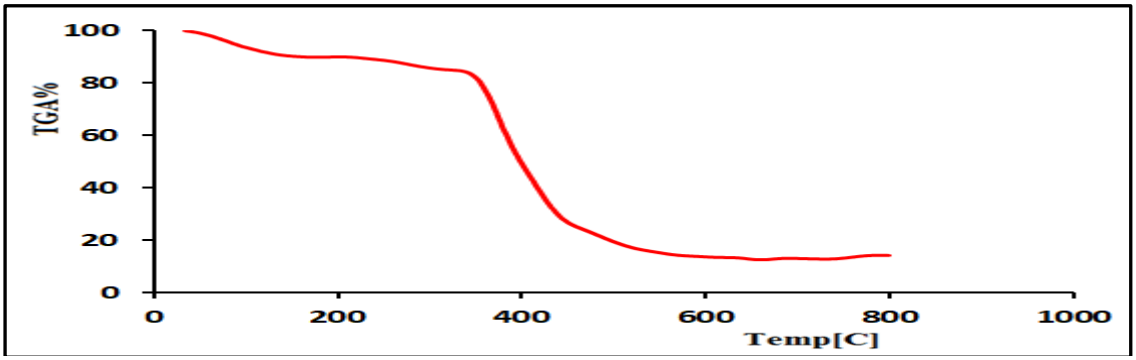

Figure 2: TG-thermograme of Co(II) complex

3.5. Catalytic hydrogenation assay

The catalytic reactivity of the Co(II) complex was tested for the reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$ as reducing agent. The reduction of 4-nitrophenol with sodium borohydride was carried out in the presence as well as in the absence of Co(II) complex. The decolorization of the test solution in the presence of Co(II) complex, indicates complete reduction of 4-nitrophenol. The time required for the reduction was 90 second. 4-nitrophenol does not get reduced in the absence of Co(II) complex [12].

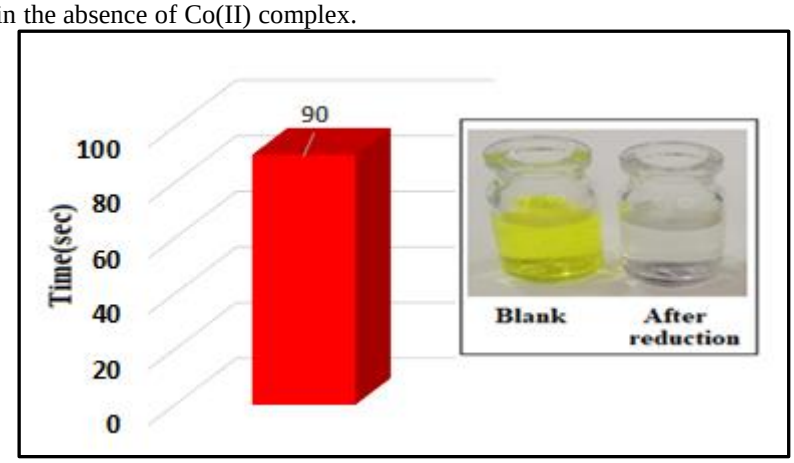

Figure 2: the color change upon reduction of 4-nitrophenol into 4-aminophenol

Conclusion

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

Acknowledgment:

The authors wish to acknowledge the valuable supports provided by Faculty of Science (Girl's), Al-Azhar University, Egypt.

Funding statements

Not applicable.

Conflicts of interest

The author declares no conflict of interest.

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Please cite this article as: **Aml M. Saleh, Omyma A.M. Ali, Zeinab H. Abd El-Wahab, Abeer A. Faheim, and Aida A. Salman** (2021). **A colorimetric new synthesized sensor Co(II) complex for pollution detection**. *International Journal of Recent Research and Applied Studies*, 8, 4(14), 127-130