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Synthesis and Characterization of Nickel (II) with Schiff base 2-Chloro-N'-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl) ethylidenebenzohydrazide

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ABSTRACT

The ligand 2-Chloro-N'-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl) ethylidenebenzo-hydrazide used to synthesize Nickel complex. The complex was characterized by elemental analysis, magnetic moment, and molar conductance along with electronic, thermal, infrared spectral analysis. Octahedral geometry has been proposed on the basis of magnetic and spectral studies.

Introduction

Recently the coordination complexes with hydrazide ligands becomes interest of researchers due to their applications in different field such as biological studies,[1,2] analytical chemistry[3],catalysis[4,5,6], clinical[7,8]. Hydrazides are important class of compounds having an azomethine -NHN=CH- Proton. When transitional metals coordinated with hydrazones they play a significant role in many catalytic reactions such as oxidation[9], cyclopropanation[10], and polymerization [11]. In view of above facts we synthesized the complex isolated from reaction of hydrazide ligand with Nickel chloride and report the structural studies of complex.

Result and discussion

The Nickel complex is brownish colored solid, stable to air and non-hygroscopic. It is insoluble in water but slightly soluble in DMSO, DMF and other organic solvents. The molar conductance values of the complex in DMSO at a concentration of 10^{-4} molar solution shows value 30 &l^{-1} which indicates non-electrolytic nature[12].

The disappearance of the entire IR band due to intra-molecular hydrogen bonding in the spectra of the complex indicates deprotonation of enolic oxygen on complex formation. The participation of enolic oxygen and azomethine nitrogen in coordination to the Nickel ion is further supported by an upward shift in v_{C-O} by 24 cm^{-1} and a downward shift in $v_{C=N}$ by 25 cm^{-1} in the complex.[13] The strong evidence of bonding is revealed by the appearance of band at 504 cm^{-1}(M-O), 459 cm^{-1}(M-N) in the spectra of the complexes.[14] A broad band present in complex in the range 3500-3400 cm^{-1} is due to v_{OH} of coordinated water[15]

The electronic spectrum of the Nickel complex exhibits three absorption bands at 11259, 16324 and 27690 cm^{-1} attributed to $^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$, $^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$, $^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ respectively indicating distorted octahedral stereochemistry[16,17]. The Nickel complex exhibit magnetic moment which is in the range 3.35 BM support the octahedral geometry[18,19].

In thermal studies, no weight loss was found on constant heating for 1 h at 120 °C which is indicative of the presence of coordinated water[20]. The TG analysis shows the percentage loss corresponding to two coordinated water molecules in complex.The loss of water in Nickel complex was found to be one-step process as only one endothermic peak was observed at190-205 °C[21].

Experimental

All the chemical and solvents used were of A.R. grade. The C, H and N contents of complexes were done on CHN analyzer. The metal contents were determined by atomic absorption spectra on Perkin-Elmer atomic absorption spectrophotometer (Model 2380). The conductivity of dilute solutions (1x10^{-4}M) in DMSO is measured on conductivity meter. Magnetic measurements at room temperature were carried out using Gouy's balance. The IR spectra of the ligands and their metal complexes were recorded on Perkin–Elmer (1430) FTIR spectrophotometer using KBr pellets. The electronic spectral measurements were made on Schimadzu UV-visible spectrophotometer (model 150).

Preparation of Nickel complex :

To a hot solution of ligand (0.02 mol) in 30 ml methanol, the Nickel chloride (0.01mol) in methanol was added drop wise. The p" of the solution adjusted about 7 to 8.5 by adding alcoholic ammonia. The reaction mixture was refluxed for about 4 hours. The respective Nickel complex separated and filtered in hot condition, washed with hot methanol followed by pet ether (40-60°C) and dried in vacuum.

Physical and analytical data of the Nickel Complexes

$[Ni(L)_2(H_2O)]$,Empirical formula : $[NiC_{36}H_{30}O_{10}N_4Cl_2O_8]$,Colour : brownish,**Yield** :81%,**CHN%**for $NiC_{36}H_{30}O_{10}N_4Cl_2O_8$; Analytical: C 53.50, H 3.74, N 6.93, Cl 8.77, Ni 7.26 ; Calculated: C 53.60, H 3.84, N 6.73, Cl 8.80, Ni 7.03.**I.R. Spectra :** 1710 $cm^{-1} v_{C=O}$, 1590 $cm^{-1} v_{C=N}$, 504 $cm^{-1} v_{M-O}$, 459 $cm^{-1} v_{M-N}$.

Conclusion

In this study we reported the synthesis of Nickel complex using 2-Chloro-N'-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl) ethylidenebenzo-Hydrazide. The structural characterization of synthesized complex made by using elemental analysis, IR and UV spectral techniques. From the spectroscopic characterization, it is concluded that metal is attached to ligand with enolic oxygen and azomethine nitrogen.

REFERENCE

1. P. V. Bernhardt, P. Chin, P. C. Sharpe, J. Y. C. Wang, and D. R. Richardson, *Journal of Biological Inorganic Chemistry*, Vol. 10, No. 7, 761–777, **2005.**
2. K. Abou-Melha and H. Faruk, *Journal of Coordination Chemistry*, Vol. 61, No. 12, 1862–1874, **2008.**

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3. Gamil Al-Hazmi, Nashwa El-Metwally, *Arabian Journal of Chemistry*, Vol. 10 (1), S1003-S10013, **2017.**
4. Xi-Shi Tai, Peng-Fei Li, Li-Li Liu, *Bulletin of Chemical Reaction Engineering & Catalysis*, 13 (1), 7-13,**2018.**
5. A. El-Motaleb and M. Ramadan, *Transition Metal Chemistry*, 30 , 471, **2005.**
6. H. Monfared, R. Bikas and P. Mayer, *Inorganic Chimical Acta*, 363, 2574, **2010.**
7. R.S. Hoonur, B.R. Patil, D.S. Badiger, R.S. Vadavi, K.B. Gudasi, P.R. Dandawate, M.M. Ghaisas, S.B. Padhye and M. Nethaji,*Europian Journal of Medicinal Chemistry*, 45, 2277, **2010.**
8. M. Gokce, S. Utku and E. Kupeli, *Europian Journal of Medicinal Chemistry*, 44,3760, **2009.**
9. C. R. Jacob, S. P. Varkey and P. Ratnasamy, Microporous and Mesoporous Materials, 22, 465, **1998.**
10. H.H.-Monfared, N.A.-Lalami, A. Pazio, K. Wozniak and C. Janiak *Inorganic Chimistry Acta*, 408, 109, **2013**.
11. R.S. George, R. Joseph, K.E. George, Inter. *journal polymer Matter*, 23, 17-26, **1993**
12. A. S. Ojo, J. N. Nwabueze, *J Pharm ChemBiolSci*, 4(2), 281-290, **2016.**
13. Percy.G.C.,Thornton.D.A., *J. Inorg. Nucl. Chem.* 34, 3357, **1972.**
14. O.W. Salawu& A.O.C. Aliyu,*Advances in Pure and Applied Chemistry*, Vol.1, 12-17, **2012**.
15. N. Kavitha, P.V. Anantha Lakshmi, *Journal of Saudi Chemical Society*, 21, 457–466, **2017**.
16. Lever, A.B.P., *Inorganic Electronic Spectroscopy*, Elsevier, New York, **1968**.
17. C.H. Kane, D. Tinguiano, F.B. Tamboura et al, Bulletin Chem. Society, 30 (1), 101-110, **2016.**
18. A. A. Alhadi, S. A. Shaker, W. A. Yehye, H. Mohd Ali, M. A. Abdullah, *Bull. Chem. Soc. Ethiop.*, 26(1), 95-101, **2012**.
19. U. L.Kala, S. Suma, M. Kurup, S. Krishnan, R. John, *Polyhedron*, 26, 1427, **2007**.
20. N. Kavitha, P.V. Anantha Lakshmi, *Journal of Saudi Chemical Society*, 21, S457–S466, **2017**.
21. Venkatesh M, phaniband M. A., *Journal of chem. pharma. Res.*, 3(2), 313-330, **2011**.

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Research Article

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Tartaric Acid: An Efficient, Catalyst for the Synthesis of Trisubstituted Imidazole under Microwave Irradiation.

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ABSTRACT

An efficient for synthesis of trisubstituted imidazole from benzil/benzoin, aromatic aldehyde and ammonium acetate in water under microwave irradiation. Tartaric acid is an inexpensive mild catalyst and the remarkable advantages such as mild reaction condition, shorter reaction time, simple procedure and excellent yield.

KEYWORDS

Trisubstituted imidazole, Tartaric acid, Water, Microwave irradiation.

1. INTRODUCTION

Nitrogen containing five membered is an important class in heterocyclic compound. Imidazole and its derivative are in a widespread range of naturally occurring molecules [1-3] and drug molecules [4-5]. Trisubstituted imidazole shows various bioactive effects such as fungicide, herbicidal [6], antitumor [7], anti-inflammatory [8], anti-allergic [9], analgesic [10], antibacterial [11] and used in biosynthesis of interleukin-1 (IL-1) [12].

Recently, several method have been developed for synthesis of trisubstituted imidazole by condensation of benzil/benzoin, aromatic aldehyde with ammonium acetate using various catalyst and reagents such as, Ionic liquid [13], Iodine [14], $ZrCl_4$ [15], NH_4OAc [16], $Yb(OTF)_3$ [17], scolecite [18], PEG-400 [19], L-Proline [20], $CuCl_3.2H_2O$ [21], and $SbCl_3$ [22].

However, some disadvantages such as tedious workup procedure, purification, use of hazardous organic solvents, expensive reagents, long reaction time, low yield, occurrence of side reaction and waste materials. The traditional methods for synthesis of trisubstituted imidazole depend upon multicomponent reaction using benzil/benzoin, substituted aromatic aldehyde and a nitrogen source.

There is a strong demand for a simple, environmentally benign, highly efficient and versatile method for one pot synthesis of trisubstituted imidazole. The present study describes synthesis of trisubstituted imidazole on reaction of benzil/benzoin, substituted aromatic aldehyde with ammonium acetate in water in presence of tartaric acid as a catalyst (Scheme-1).

2. MATERIALS AND METHODS

All chemicals, reagents and solvents were used as received from commercial source. Melting points were taken in open capillary and were uncorrected. The reaction was carried out in microwave synthesizer, Mass-II, Sineo. ^{1}H NMR spectra were recorded on a bucker DRX-300 MHz instrument and IR were recorded as KBr pellets on a Nicolet impact 410.

Scheme 1. Synthesis of trisubstituted imidazoles.

2.1. Synthesis of trisubstituted imidazole (4a-g)

A mixture of benzil/benzoin 1(1 mmol), aromatic aldehyde 2(1 mmol), ammonium acetate 3(2 mmol) and catalyst tartaric acid (10 mol %) was added in 10 ml of distilled water was irradiated under microwave oven for appropriate time (Table 2). Progress of the reaction was monitored by on TLC completion the reaction mass was poured on cold ice water. Then product was filtered, dried and recrystallized from ethanol.

3. RESULTS AND DISCUSSION

Here, we report a very simple and general method for the synthesis of trisubstituted imidazole using the catalytic amount of tartaric acid under microwave 300W (Scheme-1) as a model reaction. The synthesis of trisubstituted imidazole was carried out by condensation of benzil/benzoin, aromatic aldehyde and ammonium acetate in presence of tartaric acid as a catalyst.

To optimize the reaction conditions, all catalytic effects on the condensation reaction. The reaction was carried out in same conditions. When using PEG-400 and glycerol as catalyst, we got 4a in low yield product and prolong reaction time 86% and 92% (Table 1, Entry 1-2). Such as another catalyst [Hbim]BF_4, SSA, CAN, Yb(OTF)$_3$, L-Proline and they give low yield and more reaction time 91%, 73%, 75%, 90%, 91% yield respectively (Table 1, Entry 3-7).Hence, using Tartaric acid gives an excellent catalytic activity, which gave product in a yield of 96% (Table 1, Entry 8).

We determined the synthesis of trisubstituted imidazole derivatives using Tartaric acid at 10 mol percentage gave excellent yield of product (Table 1, entry 8). These are diprotic aldaric acid and it found naturally in plants such as bananas and grapes. It is used an antioxidant. These catalysts soluble in water, cheaper, easily available and non-hazardous. The reaction mixture was irradiated in microwave at an appropriate time (10-15 min.) the corresponding product was obtained in excellent yield.

Table 1. Comparison of different catalyst in the synthesis of Trisubstituted imidazole.

Entry	Catalyst	Time (min.)	Yield[a] (%)
1	PEG-400	360	86
2	Glycerol	180	92
3	[Hbim]BF_4	25	91
4	SSA	240	73
5	CAN	360	75
6	Yb(OTF)$_3$	120	90
7	L-Proline	540	91
8	**Tartaric acid**	**12**	**96**

[a]Reaction condition: Benzil/Benzoin(1 mmol), ammonium acetate (2 mmol), aldehyde (1 mmol) and Tartaric acid (10 mol%) at 300 W, [b]Isolated yields.

To examined the efficiency and applicability of this protocol. The reaction was carried out various substituted aromatic aldehyde are shown in Table 2. These result shows the reactions are facile electron donating and electron withdrawing substituent present on the substituted aromatic aldehyde resulting in high yields of corresponding imidazoles.

Table 2. Synthesis of Trisubstituted imidazole (4a-g) using (10 mol %) of Tartaric acid[a].

Entry	Ar-CHO	Products	Benzil Time(min.)/ Yield[b]	Benzoin Time(min.)/ Yield[b]
a			15 min./89	20 min./75
b			12 min./96	18 min./80
c			13 min./90	25 min./70
d			15 min./94	30 min./75

e	11 min./95	20 min./82
f	14 min./91	25 min./71
g	11 min./95	20 min./74

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[a]Reaction condition: Benzil/Benzoin(1 mmol), ammonium acetate (2 mmol), aldehyde (1 mmol) and Tartaric acid (10 mol%) at 300 W, [b]Isolated yields.

3.2. Characterization data

Synthesis of 2-(4-Hydroxyphenyl)-4, 5-diphenylimidazole Entry-4b**:** MP 266-268°C. IR(KBr, cm^{-1}): 3591, 3453, 3283, 3065, 1702, 1284; ^{1}HNMR (300 MHz, DMSO-d_6): 12.22 (s, 1H, NH), 9.41 (s, 1H, OH), 7.91 (d, J=8.4 Hz, 2H), 7.53-7.28 (m, 10H, Ar-H), 6.79 (d, J=8.4 Hz, 2H), ^{13}C NMR (300 MHz, DMSO-d_6): 157.5, 146.66, 127.11, 125.6, 124.4, 124.8, 114.7, 112.84, 98.56, 95.45 ppm.

Synthesis of 2-(4-Methoxyphenyl)-4, 5-diphenylimidazole Entry-4e**:** MP 229-231°C IR (KBr, cm^{-1}): 3401, 3061, 1612, 1492, 1178, 1029, 831, 760; ^{1}HNMR (300 MHz, DMSO-d_6): 12.53 (s, 1H, NH), 8.02 (d, J=8.80 Hz,2.0 Hz, 2H), 7.71-7.11 (m, 10H,Ar-H), 7.04 (dt, J=8.8Hz, 2.0 Hz, 2H), 9.82 (s, 3H, CH_3) ^{13}C NMR (300 MHz, DMSO-d_6): 158.31, 145.08, 136, 134.63, 131.39, 121.31, 127.5, 126.02, 123.08, 113.08, 54.61 ppm.

4. CONCLUSION

In summary, we have developed a simple and environmentally benign procedure for synthesis of trisubstituted imidazole using tartaric acid as a highly effective. The advantages of this method such as reduced time, mild reaction condition, desired products in excellent yield and easy workup.

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6. REFERENCES

1. Shalini, K., Sharma, P., Kumar, N. (2010) Imidazole and its biological activities: A review. *Der Chemica Sinica*, 1(3), 36-47.
2. Luca, L. D. (2006). Naturally occurring and synthetic imidazoles: Their chemistry and their biological activities. *Current medicinal chemistry*, *13*(1), 1-23.
3. Ho, J. Z., Mohareb, R. M., Ahn, J. H., Sim, T. B., Rapoport, H. (2003) Enantio specific synthesis of carbapentostatins, *J. Org. Chem.68(10),*109-114.
4. Wong, K. K. (2009). Recent developments in anti-cancer agents targeting the Ras/Raf/ MEK/ERK pathway.*Recent pat. Anticancer Drug Discovery*, *4*(2), 28-35.
5. Wolkenberg, S. E., Wisnoski, D. D., Leister, W. H., Wang, Y., Zhao, Z., &Lindsley, C. W. (2004). Efficient synthesis of imidazoles from aldehydes and 1, 2-diketones using microwave irradiation. *Organic Letters*, *6*(9), 1453-1456.
6. Maier, T., Schmierer, R., Bauer, K., Bieringer, H., Buerstell, H., Sachse, B. (2014) Substituted imidazole-5-carboxylic acid derivatives, their preparation and their use as biocides. U.S. Patent 4820335.
7. Wang, L., Woods, K. W., Li, Q., Barr, K. J., McCroskey, R. W., Hannick, S. M., ... & Warner, R. (2002). Potent, orally active heterocycle-based combretastatin A-4 analogues: synthesis, structure-activity relationship, pharmacokinetics, and in vivo antitumor activity evaluation. *Journal of medicinal chemistry*, *45*(8), 1697-1711.
8. Lombardino, J. G. (1973) Anti-inflammatory imidazole. DE Patent 2155558, 1972. U.S. 3772441.
9. Black, J. W., Durant, G. J., Emmett, J. C., & Ganellin, C. R. (1974). Sulphur-methylene isosterism in the development of metiamide, a new histamine H2-receptor antagonist. *Nature*, *248*(5443), 65.
10. Uçucu, Ü., Karaburun, N. G., & Işikdağ, İ. (2001). Synthesis and analgesic activity of some 1-benzyl-2-substituted-4, 5-diphenyl-1H-imidazole derivatives. IL *Farmaco*, *56*(4), 285-290.
11. Khan, M. S., Siddiqui, S. A., Siddiqui, M. S. R. A., Goswami, U., Srinivasan, K. V., & Khan, M. I. (2008). Antibacterial activity of synthesized 2, 4, 5-trisubstituted imidazole derivatives. *Chemical biology & drug design*, *72*(3), 197-204.
12. Gallagher, T. F., Fier-Thompson, S. M., Garigipati, R. S., Sorenson, M. E., Smietana, J. M., Lee, D., Bender P E, Lee J C, Laydon J T, Griswold D E, Chabot-Fletcher M C, Breton J J, Adams J L, & Chabot-Fletcher, M. C. (1995). 2, 4, 5-Triarylimidazole inhibitors of IL-1 biosynthesis. *Bioorganic & Medicinal Chemistry Letters*, *5*(11), 1171-1176.