



## Study of Co(AAOPD) and Cu(AAOPD) Schiff-Base Catalysts Effect in Oxidation Oximes and Carboxylic Acids Derivatives

REZA SOLEYMANI<sup>1\*</sup>, MILAD TAHERI<sup>2</sup>,  
MEHDI DARYANI<sup>3</sup> and MARZIYE HOSEYNALIBEYGI<sup>2</sup>

<sup>1</sup>Young Researchers Club, Shahre-rey Branch, Islamic Azad University, Tehran, (Iran).

<sup>2</sup>Department of Chemistry, Shahre-rey Branch, Islamic Azad University, Tehran, (Iran).

<sup>3</sup>Department of Chemistry, Damghan University, Damghan, (Iran).

\*Corresponding author E-mail: reza.soleymani@hotmail.com

(Received: February 20, 2012; Accepted: March 25, 2012)

### ABSTRACT

Oximes and carboxylic acids derivatives have a wide range in medical, pharmaceutical, agriculture industrials. Thus they have significant effects on these fields. Base-promoted or (-RC=N-) groups of cobalt and nickel groups. These were examined for oxidative process of oximes and carboxylic acids. This process is absolutely selective and in this procedure oximes transforms to aldehyde and ketone derivatives with high yield, without more oxidative process on Aldehyde group. In this mechanism high amounts of various oximes transforms into carbonyl group. However, obtained results showed that oxidative process for oximes and carboxylic acid with presence of Base-Promoted such as Co(AAOPD) and Cu(AAOPD) because of higher speed and yield. For more evaluation of reaction progress and identification of products through different methods like were used: Thin Layer Chromatography (TLC), Gas Chromatography, FT-IR, UV-Vis and elemental analysis.

**Key words:** Carboxylic acids; Oximes; Schiff-Base.

### INTRODUCTION

Publication of first report about Schiff-Base groups has more than a century history<sup>1</sup>. Schiff-Base or (-RC=N-) groups metal complexes are available directly. Commonly, a few numbers of Schiff-Base or base-promoted are used as ligand and are not available as complex. For instance, most of metal complexes with ligand H<sub>2</sub> salen directly obtained from reaction between ionic metals, salicylaldehyde and ethylenediamine<sup>2</sup>.

Interestingly that Base-Promoted properties for absorbing oxygen in organic compounds. First Schiff-Base complex was made by Jurgensen, Werner and Ettling in 1840. With reaction of copper (II) Acetate, Salicylaldehyde and Amine leads to Cu (II) salicylaldimine complex with dark green color. Schiff-Base through displacement reaction have a wide range in biological, anti-microbial, fungicide and herbicide activities. They act as ligand for complexometric process in ionic metals. They use in pigments in industrial field<sup>2,3</sup>. In fact, Schiff-

Base group are a kind of compounds which resulted from compression of aldehydes or ketone with Amine type (I) was known Imines. German chemist (Hugo Schiff) was discovered these compounds and Schiff-Base or (-RC=N-) groups, after Hugo Schiff if related Imine from reaction of one Aldehyde with Amine type (I) was produced<sup>1</sup>, call it Aldimine and if related Imine from reaction of a cotton with amine type(I) and Ammonium produced call it ketamine<sup>4</sup>. They used widely in nano-technology<sup>5,6</sup> pharmaceutical fields<sup>7,8</sup> and as artificial receptors<sup>9,10</sup> for corrosion preventing<sup>11</sup> as lignad in forming complex<sup>12</sup> chemical model for natural and complicated systems<sup>13,14</sup>, as Anti-bacterial<sup>15,16</sup> and as sensor in Poly vinyl chloride (PVC)<sup>18</sup>. Oximes abbreviation of Oxi Imine. It derivates from Aldehydes or Ketone with substitution of atom oxygen in this groups. Oximes act as protecting group for carbonyl group and act as mediators in Beckmann rearrangement. These compounds as naturally were used for pharmaceutical fields and chemical reactions in plants. All of procedures for oximes synthesis have done in solutions in which were used alcohol and water solvents. For most of these methods high temperature is necessary. Up to now, various reagents were used for oxidative process of oximes. Some instances are: Pyridinium Chlorochromate reagent<sup>19</sup>, Pyridinium Chloroformate- Hydrogen Peroxide<sup>20</sup>, 3-Methyl Ammonium Chlorochromate<sup>21</sup>, Chromic Anidride Chloro 3-Methyl Silane<sup>23</sup>, Periodic acid<sup>24</sup>, *Dinitrogen tetroxide*<sup>24</sup>, *Dimethyldioxirane*<sup>25</sup>, *Manganese triacetate*<sup>26</sup>, *tert-Butyl hydroperoxide*<sup>27</sup>, *Zirconium Sulfonyl Phosphonate*<sup>27</sup> and N-Halo Amides<sup>29</sup>. Oxidation process of carboxylic acids is a kind of de-carboxylation. In common methods of de-carboxylation, organic acid transforms to related Ketone or Aldehyde with less carbon. It was reported different catalysts<sup>30-36</sup>. However in this research, oximes and carboxylic acids in various industrials were examined for Base-Promoted catalysts of Cu(AAOPD) and Co(AAOPD) on synthesis of some derivatives of these compounds.

## EXPERIMENTAL

### General method

Applied materials were provided from Merck company (Germany) and before any experiment were purified. Thin layer

chromatography (TLC) was done with HP254. Other systems were used as follow: infrared spectrophotometer and Gas chromatography (14-A) made in Shimadzu with detector (FID) and silicon DC-200. Obtained results were recorded with Chromona software and were in integration. However, products were identified and quantified with comparison of time prevention with pure samples. All of ultraviolet spectrums were recorded with (UV-Vis), model 160 made in Shimadzu co. In addition, for identification of mentioned compounds from TLC chromatography was used that consists of fluorescent indicator with wave length of 254 nanometer which made in Merck company and then comparison of melting point and boiling point of products, IR-spectrophotometer and time prevention in gas chromatography (GC). Washing-material was used in all of experiments were solution N-Hexane and Ethyl Acetate with different ratios.

### Synthesis

#### Synthesis of Co(AAOPD) complex

*Ortho-Phenylenediamine* (0.023 mol, 2.150 g), 40 mL of ethanol solution with *Acetoacetanilide* (0.060 mol, 5.600 g) were blended for a few minutes and then (0.020 mol, 3.540 g) of *Cobalt (II) acetate* was added to  $(\text{Co}(\text{OAc})_2 \cdot 2\text{H}_2\text{O})$  and refluxed for 24 hours. Solution volume was reduced to third (1/3). In this case blue sediments of Co(AAOPD) were formed (Fig 1). Forming of sediments after 46 hours were completed in low temperatures (5 °C). Solid complex with yellow-brown color rinsed with ethanol and then dried in vacuum condition.

A yellow solid; m.p. 239-245 °C (decomp) (Aceto nitrile-DIB); IR (KBr,  $\text{cm}^{-1}$ ): 3200-3600, 3100-3500, 3150, 1650, 1580-1600, 1310, 940; MS *m/z*: 572, 544(60.03), 524(32.00), 467(52.07), 390(23.02); Anal. Calcd for  $\text{C}_{30}\text{H}_{33}\text{CoN}_4\text{O}_4$ : C, 62.93; H, 5.81; Co, 10.29; N, 9.79; O, 11.18. Found: C, 58.98; H, 6.16; Co, 11.21; N, 8.99; O, 10.89.

#### Synthesis of Cu(AAOPD) complex

*Ortho-Phenylenediamine* (0.007 mol, 0.880 g), 40 mL of ethanol with *Acetoacetanilide* (0.025 mol, 2.880 g) were blended for 5 minutes, then a yellow solution was obtained. In continued  $(\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O})$  (0.045 mol, 0.753 g) of 23 hours. Then solution volume was reduced to third (1/3)

and brown sediments of Cu(AAOPD) obtained (Fig 1). Obtained sediments after 33 hours were completed in low temperatures (5 °C). Blue solid complex rinsed with ethanol and water and then were dried in vacuum condition.

A blue dark complexes; Mp 245-263 °C (decomp) (Acetonitril-DIB); IR (KBr,  $\text{cm}^{-1}$ ): 3400-3650, 3100-3500, 3150-3250, 1500-1680, 1510, 730; MS  $m/z$ : 576, 562(20.00), 471(30.45), 470(68.09); Anal. Calcd for  $\text{C}_{30}\text{H}_{33}\text{CuN}_4\text{O}_4$ : C, 62.43; H, 5.76; Cu, 11.01; N, 9.71; O, 11.09. Found: C, 56.13; H, 6.36; Cu, 10.21; N, 9.53; O, 12.19.

### Co and Cu complex effect in synthesis Oxime and Carboxylic acid derivatives

In oxidative process of oximes, first oxidative of 4-Chloroacetophenone oxime in Acetonitrile solvent were done with presence of Dioxy Iodo Benzene (DIB) with ratios: 1 to 1/2 product yield in 78 minutes was 45%. With same condition and presence of Co(AAOPD), product yield in 40 minutes was, 94% and in presence of Cu(AAOPD) yield in so 30 minutes was 95%. In oxidative process of carboxylic acids, first oxidative of 4-hydroxy phenyl acetic acids in Acetonitrile solvent with presence of DIB were examined with ratios: 1 to 1/2. Yield in 90 minutes was 50% with same condition. But, by Co(AAOPD) catalyst, yield in 32 minutes 98% and by Cu(AAOPD) catalyst obtained yield in 48 minutes equal to 85%. As have observed presence of catalyst for reaction is necessary.

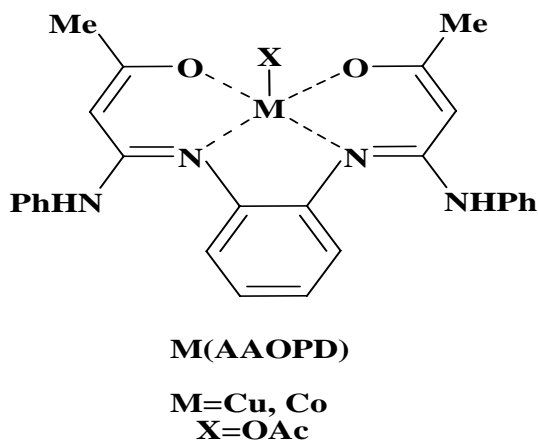


Fig.1 :M(AAOPD) structure if M=Cu, Co and X=OAc.

### Applied method for oxidative process of Oximes with presence of DIB and Cu(AAOPD) and Co(AAOPD)

0.690 mmol of various oximes into a bulb (25 mL) containing of 2.000 mL Acetonitrile, 0.005 mmol of catalyst and 0.050 mmol of Imidazole added and this reaction by magnetic agitator was done in room temperature. Then, 0.150 mmol of DIB was added to above mixture and continues mixing. Reaction progress was recorded TLC chromatography.

### Applied method for oxidative process of Carboxylic acids with presence of DIB and Co(AAOPD) and Cu(AAOPD)

0.690 mmol of various carboxylic acids in to a bulb (25 mL) containing of 2.000 mL acetonitrile were added with 0.008 mmol of catalyst and 0.090 mmol of imidazole and this reaction with magnetic agitator was done in room temperature. Then 0.150 mmol of DIB added to above mixture and continued mixing. Reaction progress was recorded by TLC chromatography.

## RESULTS AND DISCUSSION

In this research, Co(AAOPD) and Cu(AAOPD) have significant influence on synthesis and oxidative of Oximes and Carboxylic acids with DIB. From oxidative process of Oximes, obtain Aldehydes and Ketone. In this reaction Aldoximes and Ketoximes transforms to primary Carbonyl with presence of Schiff-Base non-carbonyl compounds

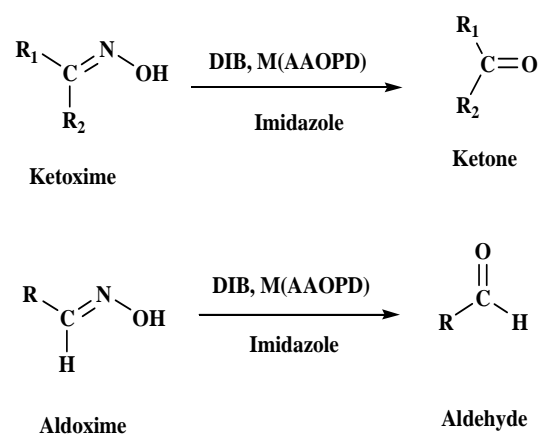


Fig. 2 :Synthetic route for the synthesis oxime derivatives.

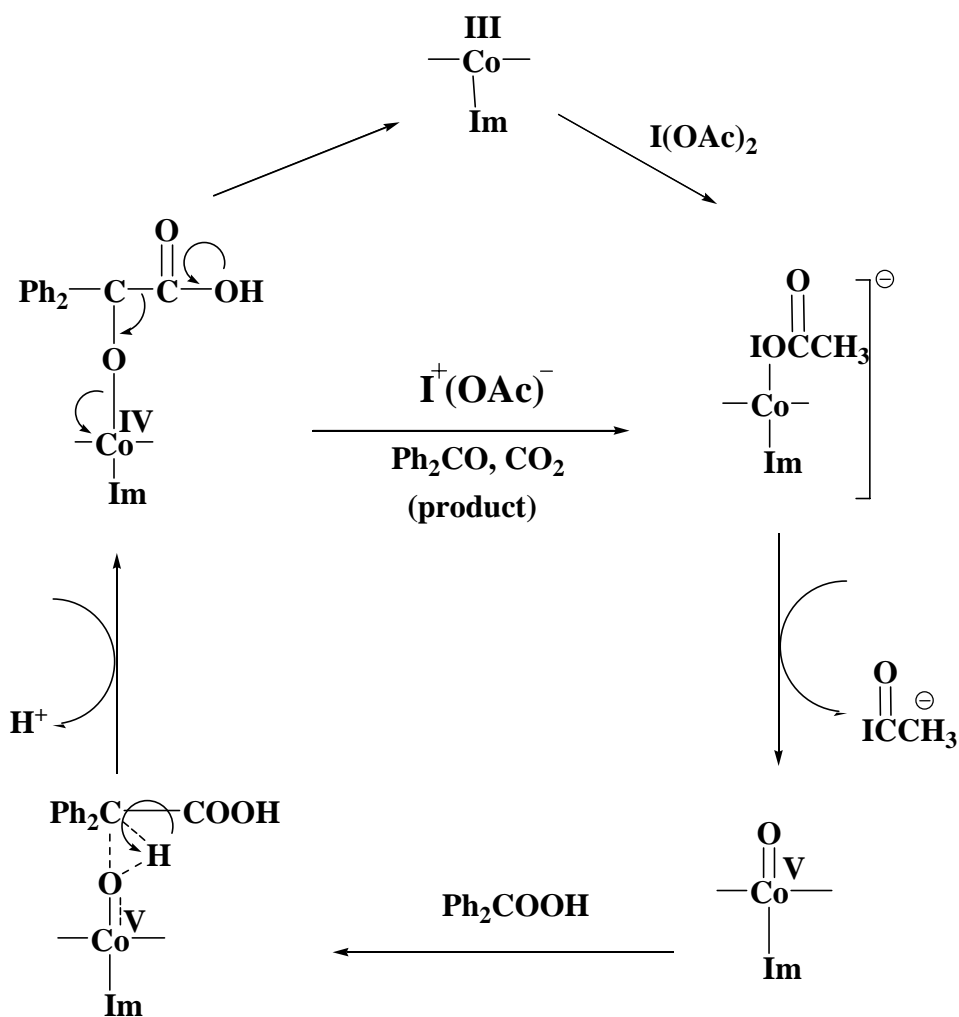


Fig. 3 : The proposed mechanism for synthesis different Carboxylic acid derivatives.

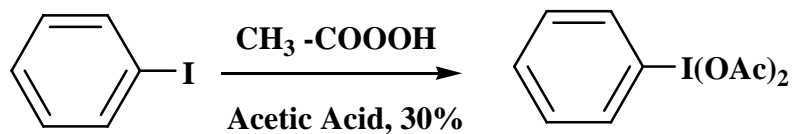
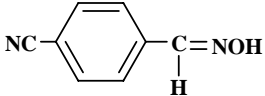
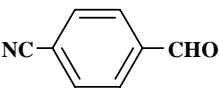
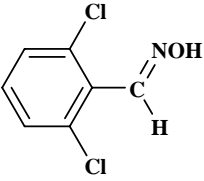
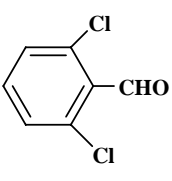
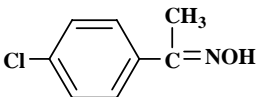
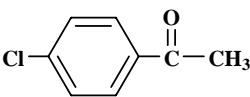
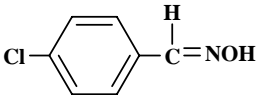
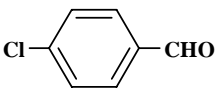
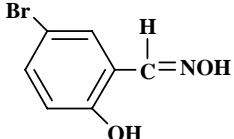
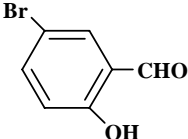
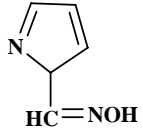
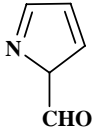
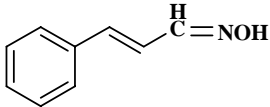
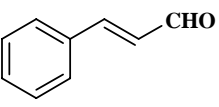
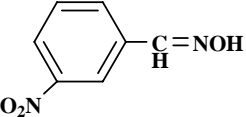
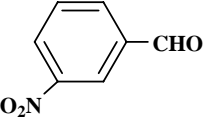
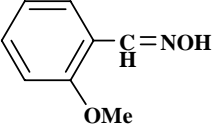
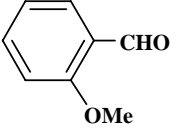
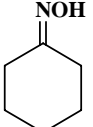
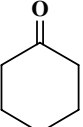


Fig.4: Synthetic route for the synthesis Diiodo Benzene (DIB) structure.

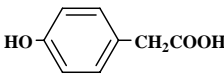
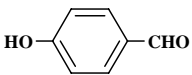
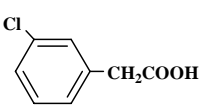
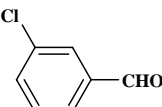
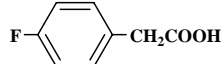
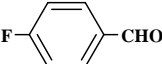
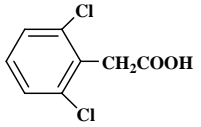
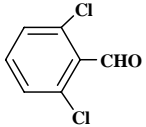
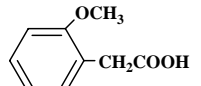
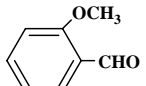
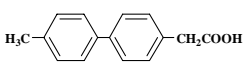
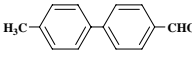
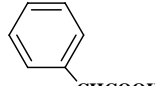
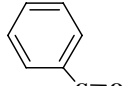
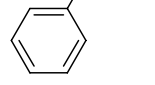
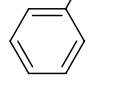
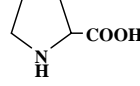
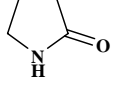
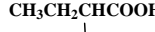
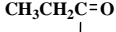


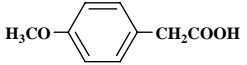

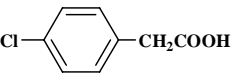
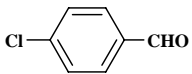
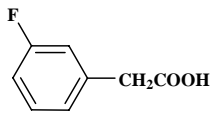
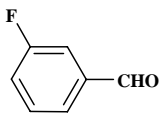
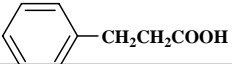
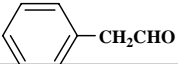
**Table 1: Yields and reaction conditions of the synthesized Oxime derivatives that catalyzed by Co(AAOPD) compound in room temperature and Acetonitrile solvent.**

Entry	Substrate	Product	Melting Point	Yield (%)	Time (min)
1			Liquid	80	50
2			78	89	35
3			20	85	48
4			43	87	42
5			Liquid	81	30
6			Liquid	93	75
7			Liquid	91	53
8			Liquid	90	45
9			Liquid	81	39
10			Liquid	83	43

**Table 2: Yields and reaction conditions of the synthesized Oxime derivatives that catalyzed by Cu(AAOPD) compound in room temperature and Acetonitrile solvent.**

Entry	Substrate	Product	Melting Point	Yield (%)	Time (min)
1			15	82	15
2			35	90	10
3			52	91	45
4			18	98	36
5			23	85	12
6			82	99	66
7			13	98	10
8			19	92	12
9			15	84	14
10			10	89	15

**Table 3 : Yields and reaction conditions of the synthesized Carboxylic acid derivatives that catalyzed by Co(AAOPD) compound in room temperature and Acetonitrile solvent.**

Entry	Substrate	Product	Melting Point	Yield (%)	Time (min)
1			19	82	175
2			Liquid	84	270
3			Liquid	89	300
4			68	89	380
5			43	90	250
6			Liquid	81	240
7			48	75	205
8			Liquid	45	360
9			Liquid	79	275
10			Liquid	92	360
11			43	90	320
12			Liquid	80	320
13			Liquid	-	285
14			Liquid	35	300
15			Liquid	40	385

**Table 4 :Yields and reaction conditions of the synthesized Carboxylic acid derivatives that catalyzed by Cu(AAOPD) compound in room temperature and Acetonitrile solvent.**

Entry	Substrate	Product	Melting Point	Yield (%)	Time (min)
1			20	90	220
2			Liquid	55	295
3			Liquid	75	312
4			68	82	430
5			30	91	288
6			Liquid	90	265
7			48	60	214
8			Liquid	84	385
9			Liquid	93	294
10	$\text{CH}_3\text{CH}_2\text{CHCOOH}$	$\text{CH}_3\text{CH}_2\text{C=O}$	Liquid	80	390
11			44	81	375
12			Liquid	55	365
13			Liquid	78	325
14			Liquid	86	360
15			Liquid	88	430



like, Olefins, Esters, Nitrils, Nitro groups, Nitrite groups, alcohols and aliphatic amines type (I) leads to obtain Oximes. This compounds with strong oxidatives like  $\text{CrO}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{KMnO}_4$  transforms to Carbonyl group and then to acid. If oxidation goal is production of carbonyl group must use of soft oxidative. In this study oxidative process of various Oximes have done by a new oxidative DIB. This compound is a selective, soft, nontoxic and favourable for oxidative process of Oximes. Products with presence of Co(AAOPD) and Cu(AAOPD) in Acetonitril solvent transforms to Carbonyl group with high yield (Fig 2). Oxidative of 4-Chloro benzaldehyde Oxime in room temperature with different molar ratios. Oxidative process of 4-Chlorobenzaldehyde Oxime, 4-chloroacetophenone oxime, 4-cyanobenzaldehyde oxime in presence of DIB, our evaluations with Co(AAOPD) or Cu(AAOPD). Obtained results show that in refluxed condition and in room temperature has no significant effect on productions. For more information refer to (1-4) tables. The oxidation of Oximes in normal temperatures with molar ratios: 1: 10: 20: 25 of catalyst to Imidazole leads to Aldehydes and Ketones with presence of DIB. According to previous studies, oxidative process of Alkenes by mediator metal complexes leads to parameters like (M=O). In this catalyst system forming of a same mediator also is necessary. Thus de oxidation and de carboxylation by Cu(AAOPD) and Co(AAOPD)

have done through Co=O and Cu=O. There is a simple mechanism for the decarboxylation as shown in Fig 3. DIB consists of two Acetoxy group bonded to ph-I obtaining this is very easy (Fig 4). These properties cause DIB be an available for oxidative process of carbonyl groups.

## CONCLUSION

Our research showed that with Co(AAOPD) and Cu(AAOPD), a kind of soft oxidant, non-toxic and effective for oxidative process of oximes of Aldehydes and Ketones derivatives with high yield. Various Oximes transform to Carbonyl derivative with high percentages. In these reaction, Oximes with presence of Cu(AAOPD) has higher speed yield than Co(AAOPD). Carboxylic acids with presence of Co(AAOPD) with higher speed transform to Carbonyl group and yield percentages has not significant change with variation of catalysts. Our studies predicts that (M=O) with high capacity is most important parameter for oxidation in acids.

## ACKNOWLEDGEMENTS

The authors are indebted to missy Rezvan Soleymani for their interest in this work and many helpful discussions. This work was supported by Islamic Azad University Shahre-rey branch.

## REFERENCES

1. H. Schiff, *Ann. Supp*, **151**: 186 (1864).
2. F.P. Dwyer, D.P. Mellor, *Chelating Agent and Metal Chelates*, Academic, London, (1964).
3. J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Book, California, (1987).
4. R.D. Jones, D.A. Summervill, *F. Basolo*, **79**: 139 (1979).
5. A. Shatkey, *Anal. Chem*, **39**: 105 (1967).
6. S. Khalil, *Analyst*, **124**: 139 (1999).
7. F. Hofmeister, *Arch. Exp. Pathol. Pharmacol*, **24**: 247 (1888).
8. A. Graggs, G.J. Moody, J.D.R. Thomas, *J. Chem. Educ*, **51**: 541 (1974).
9. W. E. Morf, W. Simon, *Helv. Chim. Acta*, **69**: 1320 (1986).
10. E. Bakker, P. Buhlmann, E. Pretsch, *Chem. Rev*, **97**: 3083 (1997).
11. D. Ammann, R. Bissig, M. Guggi, E. Pretsch, W. Simon, I.J. Borowitz, L. Weiss, *Helv. Chem. Acta*, **58**: 1355 (1975).
12. M. Huser, W.E. Morf, K. Fluri, K. Seiler, P. Schulthess, W. Simon, *Helv. Chim. Acta*, **73**: 1481 (1990).
13. G. Horvai, *Trend. Anal. Chem*, **16**: 260 (1997).
14. E. Bakker, *Anal. Chem*, **69**: 1061 (1997).
15. E. Bakker, E. Pretsch, P. Buhlmann, *Anal. Chem*, **72**: 1127 (2000).
16. G.G. Guilbault, R.A. Durst, M.S. Frant, H.

- Freiser, E.H. Hansen, T.S. Light, E. Pungor, G. Rechnitz, N.M. Rice, T.J. Rohm, W. Simon, J.D.R. Thomas, *Pur. Appl. Chem*, **48**: 127 (1976).
17. Mohit Kumar and Shamim Ahmad, *Orient. J. Chem.*, **26**(4); 1455-1459 (2010).
18. A. Jyo, R. Minakami, Y. Kanda, E. Egawa, *Sensors, and Actuators B*, **13**: 2001 (1993).
19. J.R. Maloney, R.E. Lyle, J.E. Scavendra, G.G. Lyle, *Synthesis*, **212** (1978).
20. J. Drabowicz, *Synthesis*, **125** (1980).
21. C.G. Rao, A.H. Radhakrishna, B.B. Singh, S.P. Bhatnagar, *Synthesis*, **808** (1983).
22. J.M. Aizpurua, M. Juaristi, B. Lecea, C. Palmo, *Tetrahedron*, **41**: 2903 (1985).
23. H.C. Araujo, G.A.L. Ferriera, J.R.D. Mahajan, *Chem Soc*, **1**: 2257 (1974).
24. S.B. Shim, K. Kim, Y.H. Kim, *Tetrahedron Lett*, **28**: 645 (1987).
25. G.A. Olah, Q. Liao, C.S. Lee, G.K. Surya Prakash, *Synlett*, **8**: 427 (1993).
26. H.D. Ayhan, E.A. Tanyeli, *Tetrahedron Lett*, **38**: 7267 (1997).
27. N.B. Barhate, A.S. Gajare, R.D. Wakharkar, A. Sudalai, *Tetrahedron Lett*, **38**: 653 (1997).
28. M. Curini, O. Rosati, E. Pisani, *Synlett*, **333** (1996).
29. B.P. Bandgar, L.B. Kunde, J.L. Thote, *Synth. Commun*, **27**: 1149 (1997).
30. V. Mirkhani, S. Tangestaninejad, M. Moghadam, M. Moghbel, *Bioorganic & Medicinal Chemistry*, **12**: 903 (2004).
31. J.T. Groves, T.E. Nemo, *J. Am. Chem. Soc*, **105**: 5786 (1983).
32. B. Meunier, *Bull. Soc. Chim. Fr*, **4**: 578 (1986).
33. H. Sugimoto, H.C. Tung, D.T. Sawyer, *J. Am. Chem. Soc.* **110**: 2465 (1988).
34. D. Mansuy, *Pure. Appl. Chem*, **59**: (1987) 579.
35. D. Mansuy, P. Battioni, J.P. Battioni, *Eur. J. Biochem*, **184**: 267 (1989).
36. O. Bartolini, B.J. Meunier, *Chem. Soc., Perkin Trans*, **2**: 1967 (1984).