THE EXPERIMENT
INTERNATIONAL JOURNAL OF SCIENCE AND TECHNOLOGY

ISSN-2319-2119

RESEARCH ARTICLE

Adedibu C. Tella et al, The *Experiment, 2013 Vol. 16(2), 1123-1129*

SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES OF BIS(2-HYDROXY-4-METHOXYACETOPHENONE) ETHYLENEDIIMINE

ABSTRACT

Four Schiff-Base complexes of Cu(II), Co(II), Ni(II) and VO(IV) derived from Bis(2-hydroxy-4-methoxyacetophenone) ethylenediimine were synthesized. The Schiff-base (ligand) was formed by the 1:2 molar condensation of ethylenediamine with 2-hydroxy-4-methoxyacetophenone. The complexes were characterized by the elemental analysis, infrared and electronic spectra. The 2-hydroxy-4-methoxyacetophenone ethylenediamine was found be tetradentate ligand. Cu(II), Co(II) and Ni(II) coordinate with the ligand through both oxygen of the phenoxyl group and nitrogen of C=N azomethine to give square planar geometry except Co(II) which gave tetrahedral geometry. VO(IV) also coordinates using the same sites like other metals but gave tetragonal pyramidal configuration.

key words Schiff-base, Condensation, Infra-red spectra , 2-hydoxy-4-methoxyacetophenone

INTRODUCTION

Compounds containing an azomethine group (-CH=N-) are known as Schiff-bases. Schiff bases are generally bi, tri, tetra-dentate ligands capable of forming very stable complexes with transition metals. Tetradentate Schiff bases with a N_2O_2 donor atom set are well known to coordinate with various metal ions and this has attracted many authors[1-3]. Schiff base complexes have been studied for their dioxygen uptake[4] and oxidative catalysis[5], insertion of oxygen into organic substrate[6-7].

The complexes of transition metal(II) which involves derivatives of salicyaldehyde and diamine, acetophenone and diamine are the subject of many authors[2,7]. The present study aimed to investigate the reaction of tetradentate Schiff base derived from condensation of ethylenediamine with substituted acetophenone (2-hydroxy-4-methoxyacetophenone) with Cobalt, Copper, Nickel and Oxovanadium ions. The prepared ligand and complexes were characterized by elemental analysis, UV-visible and infrared spectroscopies.

EXPERIMENTAL

Materials and Methods

2-hydroxy-4-methoxyacetophenone and ethylenadiamine were purchased from sigma chemical Co. (USA). All other solvents and reagents were of high purity (Aldrich and sigma) and were used without further purification. The metal salts used for complexation: Copper(II) acetate monohydrate; Cobalt(II) acetate tetrahydrate; Nickel(II) sulfate hexahydrate; Vanadylsulfate monohydrate were obtained from British Drug House (BDH) Chemical Limited Company. Analytical measurements were carried out in Micro Analytical Laboratory of the Department of Chemistry, University of Manchester, U.K. The Infra red (IR) spectra were recorded on a Pekin-Elmer infrared spectrophotometer with KBr pellets in range 4000 – 250cm^{-1} at the University of Zululand, South Africa. The UV-Vis spectra (in Chloroform) of the complexes were done in HEλ10β UV-Visible spectrophotometer V4.55. The melting points were determined using liquid paraffin and complexometric titration was used to determine the percentage metal content in the complexes of Cu(II), Co(II) and Ni(II) while percentage metal in VO(IV) complex was estimated gravimetrically.

Preparation of the Schiff base : (Bis(2-hydroxy-4-methoxyacetophenone) ethylenediimine [(2H – 4 - MA)$_2$en])

The Schiff base ligand was prepared by condensation of 2-hydroxy-4-methoxyacetophenone (25ml, 16.618g, 0.1 mole) with (25ml, 3.005g, 0.05mole) of ethylenediamine in ethanol. The resulting mixture was stirred for 1 hour at 40-50°C. The pale yellow precipitate formed was filtered, washed several times using deionized water, washed with methanol and dried over anhydrous calcium chloride in a

THE EXPERIMENT
INTERNATIONAL JOURNAL OF SCIENCE AND TECHNOLOGY
ISSN-2319-2119
RESEARCH ARTICLE
Adedibu C. Tella et al, The *Experiment, 2013 Vol. 16(2), 1123-1129*

dessicator. The equation of the reaction is shown in figure 1.

Yield : 83.92%, Mwt=356.43; M.pt 190-192°C, Anal. Calcd for $[C_{20}H_{24}O_4N_2]$: C67.40; H6.79; N7.86, Found: C:68.23; H6.64; N7.80.IR(KBr cm^{-1}) 2857, 1584, 1516, 1450, 1336, 1250, 1206, 1134, 1059, 970, 827.

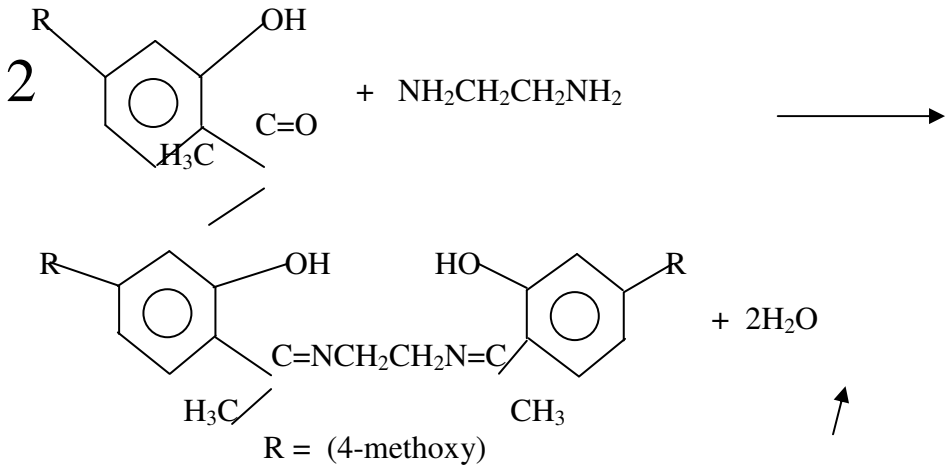


Fig. 1: Structural representation of the Schiff bases (ligand)

Synthesis of Complexes

Compound 1 : [Cu(4-MA)$_2$en]. 3/2H$_2$O

The complex was prepared by the addition 0.998g(5mmol) $Cu(CH_3COO)_2.H_2O$ (in 20ml de-ionized water) into a stirring solution 1.782g (5mmol) of the ligand (in 40ml hot methanoic solution). The resulting purple solution formed was refluxed for an hour and cooled to room temperature. The purplish precipitate obtained was filtered, washed with methanol and dried. A purple powdered was obtained.

Yield: 98%, M.wt = 444.97, m.p>205°C, Anal.Calcd for $C_{20}H_{25}O_{5.5}N_2.Cu$: C53.99; H5.66; N6.30; CU 14.28, Found : C54.49; H5.71; N6.36; Cu14.58. IR(KBr cm^{-1}) 3437, 1607, 1580, 1526, 1447, 1352, 525, 517, 488, 459. UV-Vis(chloroform) λnm: 554, 396.

The formation of the complexes may be represented by the general equation thus:

$$MX_2.nH_2O + PQ - H_2 \xrightarrow[\text{de-ionized water}]{\text{methanol}} MPQ.nH_2O + 2HX$$

$PQ - H_2$ = dibasic tetradentate Schiff base

X_2 = halide

Compound 2 : [Co(4-MA)$_2$en].H$_2$0

0.747g(3mmol) of $Co(CH_3COO)_2.4H_2O$ in 15ml de-ionized water was added to 1.069g(3mmol) of stirring solution of the [Bis(2H-4-MA)$_2$en] in 20ml hot methanol. The brownish solution formed was refluxed for one hour and the precipitate formed was isolated by filtration, washed with methanol and dried at room temperature. The brown solid powder was obtained.

Yield: 49%, M.wt=431.36, M.pt >205°C. Anal.calcd for $C_{20}H_{24}O_5N_2Co$: C55.69; H5.61; N=6.49; Co13.66. Found: C55.54; H5.93;

THE EXPERIMENT
INTERNATIONAL JOURNAL OF SCIENCE AND TECHNOLOGY

ISSN-2319-2119

RESEARCH ARTICLE

Adedibu C. Tella et al, The *Experiment, 2013 Vol. 16(2), 1123-1129*

N6.13; Co14.64. IR(KBr cm-1) 3456, 1607, 1568, 1512, 1447, 1387, 521, 519, 491, 479. UV-Vis(chloroform) λnm : 632, 470, 423

Compound 3 : [Ni(4-MA)$_2$en].3/2H$_2$O

1.782g(5mmol) of Bis[(2H-MA)$_2$en] dissolved in 30ml hot methanolic solution was added to 1.314g(5mmol) of $NiSO_4.6H_2O$ in 20ml de-ionized water. The resulting solution was stirred. 0.984g(12mmol) of CH_3COONa in 10ml de-ionised water was added to raise the pH. The pinkish brown solution formed was refluxed for an hour. The pinkish brown precipitate formed was cooled, filtered and washed-free of sulphate with de-ionised water followed by washing with methanol and dried at room temperature. A pinkish brown powder was obtained. Yield: 90.40%, Mwt = 440.14; M.pt > 205°C. Anal.calcd for $C_{20}H_{25}O_{5.5}N_2Ni$: C54.58; H5.73; N6.36; Ni 13.34. Found : C 54.90, H5.53; N6.30; Ni 13.07. IR(KBr cm^{-1})3447, 1607, 1578, 1526, 1450, 1358, 519, 484, 476. UV-Vis(chloroform) λnm : 558,429.

Compound 4: [VO(4-MA)$_2$en]. ½H$_2$O

0.978g(6mmol) of $VOSO_4.H_2O$, 2.139g(6mmol) of Schiff base ligand and 0.984g(12mmol) of CH_3COONa were dissolved in 30ml de-ionized water, 50ml hot methanol and 20ml de-ionized water respectively. $VOSO_4.H_2O$ solution was gradually added to stirring solution of the ligand followed by addition of CH_3COONa solution. The mixture was kept warm and stirred for 30minutes. The pale green precipitate formed was isolated by filtration, washed free of sulphate with de-ionised water followed by washing with methanol and dried at room temperature. A pale green powder was obtained.

Yield: 65.40%, Mwt = 430.36; M.pt > 205°C. Anal.calcd for $C_{20}H_{23}O_{5.5}N_2$-V: C55.82; H5.39; N6.51; V11.83. Found : C55.70, H5.36; N6.50; V10.82. IR(KBr cm^{-1})3483, 1601, 1574, 1524, 1441, 1305, 978, 853, 519, 503, 479, 450. UV-Vis(chloroform) λnm : 556, 461, 400.

RESULTS AND DISCUSSION

The elemental analyses agreed well with 1:1 metal to ligand stoichiometry for all the complexes. The complexes are of various colours varied from purple, pale green to brownish colour different from the colour of the ligand indicating that the colours formed depend on the metal ions. The melting points of the complexes are different (higher) than that of the Schiff base ligand, an evidence for complexation. All complexes were soluble in ethanol, methanol, chloroform, acetone, water, and dimethylformamide except few as shown in Table 1. In all the complexes Bis(2-hydroxyl-4-methoxyacetophenone)ethylenediimine acts as a tetradentate ligand and binds through the oxygen of the phenoxyl group and nitrogen of C=N azomethine to give square planar and tetrahedral geometries while VO(IV) gave tetragonal pyramidal geometry.

Infrared Spectra

The importance bands in the IR spectra of the Schiff base ligand [Bis(2-hydroxy-4-methoxyacetophenone)ethylenediimine] as well as complexes as shown in Table 2 and figure 2. In the IR spectra of the ligand [(2H-4-MA)$_2$en], a weak broad band at 3000 – 2875cm^{-1} which has been assigned to the intramolecularly hydrogen bonded phenolic-OH in the spectra of the ligand is not observed in the IR spectra of these complexes. There is no corresponding band in the metal complexes. A broad band around 3400 – 3500cm^{-1} in all the complexes can be assigned to the O-H vibrations of lattice water molecules[12,23].

The free ligand also exhibited strong band at 1584cm^{-1} which undergone a slight hypsochronic shift in the complexes and this was assigned to V(C=N) stretching[8-9]. This band was shifted to higher frequency by 17-23cm^{-1} as compared to the ligand. This suggest the involvement of azomethine group(C=N) in the coordination with the metal ions and bonded through the Nitrogen atom[10-12]. The band due

ISSN-2319-2119

RESEARCH ARTICLE

Adedibu C. Tella et al, The *Experiment, 2013 Vol. 16(2), 1123-1129*

to phenolic C-O stretching vibration that appeared in 1336cm^{-1} in the Schiff base has shifted towards higher frequency by Ca 14-51cm^{-1} in the

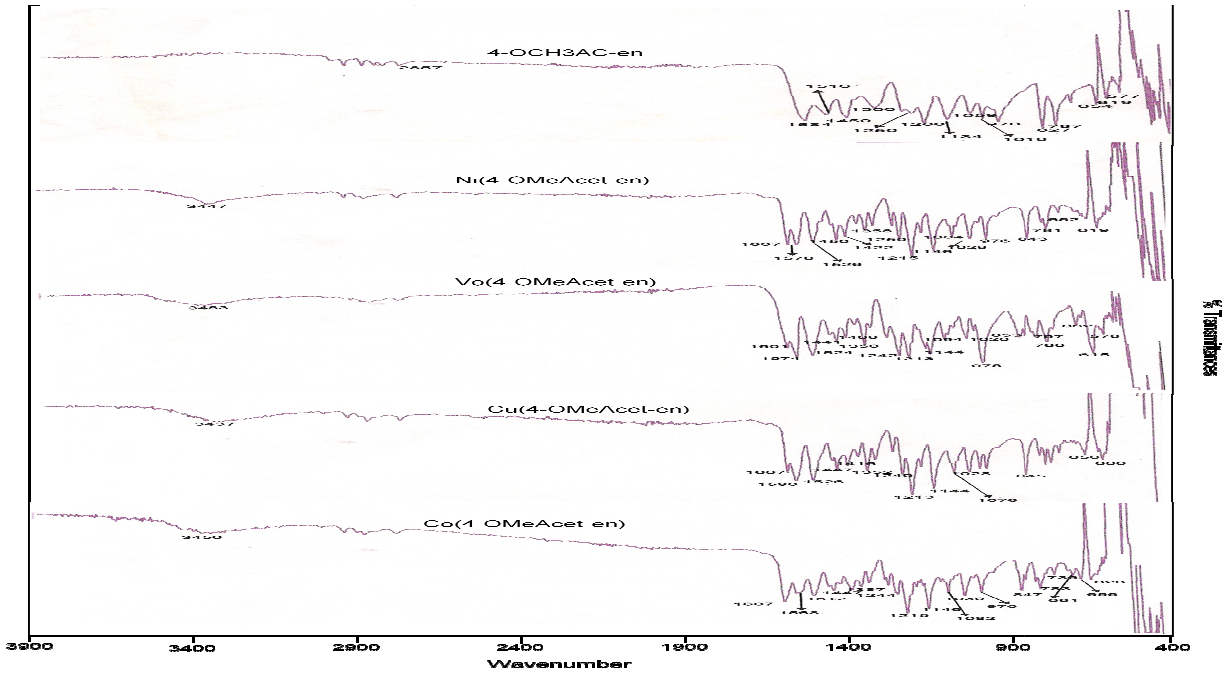


Figure 2: IR Spectra of Ligand and Complexes

complexes. The positive shift of the band suggests the coordination of the phenolate anions with the metal ions via deprotonation[13]. The shift equally confirms the participation of oxygen in the C-O-M bond[14]. The ring skeletal vibrations (C=C) were consistent in all derivatives and unaffected by complexation. In the low frequency region, the new absorption bands observed in the complexes in the region 476-491cm^{-1} and 519-521cm^{-1} were attributed to V(M-phenolic-O) and (M-N) respectively[15-16]. The M-O and M-N stretching vibration provide direct evidence for the complexation. A very sharp peak at 978cm^{-1} suggests the presence of V = O bond in VO(IV) complex. The value is in the range observed for monomeric VO^{2+} complexes[17]. All the IR data suggest that the metal is bonded to Schiff base through the phenolic oxygen and the imino Nitrogen[18].

Electronic Spectra

The UV-visible spectra of the complexes are shown in Table 3. The electronic spectra of Cu(II) complex in chloroform consists of two bands 396(25,253) and 554(18,051). These were assigned to $^2Bg \longrightarrow {}^2Eg$ and $^2B_1g \longrightarrow {}^2A_1g$ respectively. The spectra pattern suggested a square planar geometry around the copper(II) ion[7,18]. The solution spectra data of Co(II) complex consisted of three bands: 423(23,641), 470(21,277) and 632(15,823). 470nm and 632nm were assigned to $^4T_1g \longrightarrow {}^4T_1g(P)$ and $^4T_1g \longrightarrow {}^4A_2g$ respectively. The band at 423(23,641) is considered as shoulder band and was also assigned to $^4T_1g \longrightarrow {}^4T_2g$. [19,20].

The spectra of Ni(II) complex consists of two bands in the range between 558nm and 429nm(17,921 and 23,310)cm-1 and were assigned $^3T_1(F) \longrightarrow {}^2A_2(F)$ and $^3T_1(F) \longrightarrow {}^3T_1(P)$ respectively. This is a probable indicative of four coordinate square planar geometry[21]. The brownish yellow colour of the complexes, its diamagnetism and the position of electronic absorption bands of medium intensity are characteristics of low-spin square planar Ni(II) complexes[7].

THE EXPERIMENT
INTERNATIONAL JOURNAL OF SCIENCE AND TECHNOLOGY

ISSN-2319-2119

RESEARCH ARTICLE

Adedibu C. Tella et al, The *Experiment, 2013 Vol. 16(2), 1123-1129*

Three bands were observed in the spectra of oxovanadium(IV): 556(17,668), 461(21,692) and 400(25,000). These are classified as band II (17,668cm^{-1}) and Band III (21,692, 25,000)cm^{-1} and were assigned ($b_2 - b_1^*$) and ($b_2 - a_1^*$) transitions respectively[22]. The five-coordinated Schiff base complex of VO^{2+} may have the usual tetragonal pyramidal structure[17].

In all the complexes Bis(2-hydroxyl-4-methoxyacetophenone)ethylenediimine acts as a tetradentate ligand and binds through the oxygen of the phenoxyl group and nitrogen of C=N azomethine to give square planar and tetrahedral geometries while VO(IV) gave tetragonal pyramidal geometry. The proposed structures are presented in figures 3 and 4.

COMPLEXES	ETHANOL		METHANOL		CHLOROFORM		TOLUENE		WATER		ACETONE		DMF	
	C	H	C	H	C	H	C	H	C	H	C	H	C	H
[Cu(4-MA)$_2$en]	SS	S	SS	SS	S	S	SS	S	IS	IS	S	S	S	S
[Co(4-MA)$_2$en]	SS	S	SS	S	S	S	S	S	SS	SS	S	S	S	S
[Ni(4-MA)$_2$en]	SS	SS	SS	SS	S	S	S	S	S	S	SS	S	S	S
[VO(4-MA)$_2$en]	SS	S	SS	S	S	S	SS	SS	IS	IS	SS	SS	S	S

Table 1: Solubility data of the complexes

S – Soluble, IS – Insoluble, H – Hot, SS – Sparingly soluble, C – Cold, DMF – Dimethyl formamide

Complexes/Ligand	ν(OH) hydrogen bonded	(H_2O)/ lattice water	ν (C=N)	ν (C=C)aromatic	ν (phenolic C=O)	ν (M-N)	ν (M-O)
[Bis(2H-4MA)$_2$en]	3000 - 2857	-	1584	1516, 1450	1336	-	-
[Cu(4-MA) $_2$en].3/2H_2O		3437	1607	1580, 1526, 1447	1352	525	488
[Co(4-MA) $_2$en].H_2O		3456	1607	1568, 1512, 1447	1387	521	491
[VO(4-MA) $_2$en].½H_2O		3483	1601	1574, 1524, 1441	1350	519	479
[Ni(4-MA) $_2$en].3/2H_2O		3447	1607	1578, 1526, 1450	1358	519	476

Table 2: Infrared Spectra of [Bis(2-hydroxy-4-methoxyacetophenone) ethylenendiimine] and its complexes (cm^{-1})

Complexes	λ_{max}nm(λ_{max}cm^{-1}) in chloroform
[Cu(4-MA)$_2$en]	554(18,051), 396(25,253)
[Co(4-MA)$_2$en]	632(15,823), 470(21,277), 423(23,641)
[Ni(4-MA)$_2$en]	558(17,921), 429(23,310)
[VO(4-MA)$_2$en]	556(17,668), 461(21,692), 400(25,000)

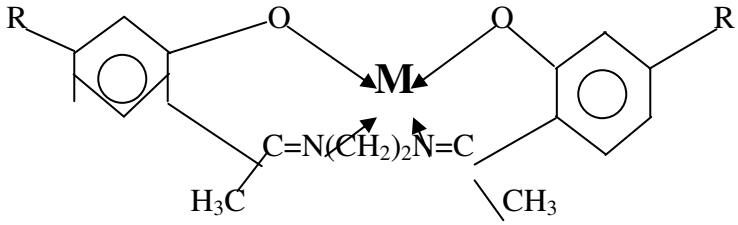
Table 3 : Electronic Spectra data of the Schiff Base complexes

THE EXPERIMENT
INTERNATIONAL JOURNAL OF SCIENCE AND TECHNOLOGY

ISSN-2319-2119

RESEARCH ARTICLE

Adedibu C. Tella et al, The *Experiment, 2013 Vol. 16(2), 1123-1129*



M = Cu(II), Ni(II), Co(II), R = OCH_3

Figure 3. Proposed structure metal complexes of (4-MA)$_2$en

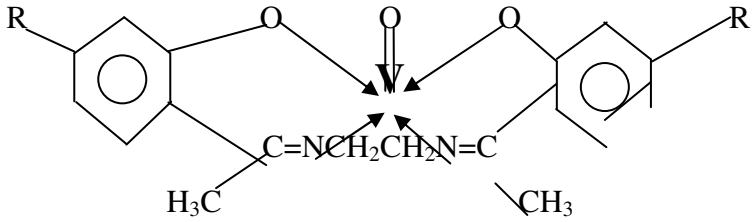


Figure 4 : Proposed structure V(IV) complex of (4-MA)$_2$en

CONCLUSION

Four complexes of Bis(2-hydroxy-4-methoxyacetophenome)ethylenediimine were synthesized and isolated. They were characterized using Elemental analysis, IR and UV Spectroscopies. The complexes isolated have square planar, tetrahedral and tetragonal pyramidal geometries. The Schiff base ligand acts as a tetradentate ligand and binds to metal ions through phenolic oxygen and the imino nitrogen.

REFERENCES

1. Siddiqui, R. A.; Raj, P.; Saxena, A.K.. Synth. React. Inorg. Met. Org. Chem. 1996, 26, 1189
2. Ramesh, R.; Suganthty, P.K.; Natarajan, K. Synth. React. Inorg. Met. Org.Chem. 1996, 26, 47-60
3. Atkins, R.; Breweg, G.; Kakot, E.; Mockler, G. M.; Sinn, E. Inorg. Chem. 1985, 24; 127
4. Tovrog, B.S. ; Kitko, D.J.; Drago, R.S. J. Am. Chem. Soc. 1976, 98, 5144.
5. Kessel, S.L.; Emberson, R.M; Debunner, P.G.; Hendrickson, D.N. Inorg. Chem 1980, 19, 1170.
6. Dixit, P.S.; Srinivason, K. Inorg. Chem. 1968, 27, 4507
7. Mokhles, M.A. ; Jour. Chinese Chem. Soc. 2001, 48, 153-158
8. Bukhari, H. I.; Arif, M.; Akbar, J.; Khan, A.H. Pakistan J. Biol. Sc. 2005 8(4), 614-61
9. Basavaraju, B. ; Bhojya Nalk, H.S.; Prabhakasa, M.C. E-journal Chemistry 2007 4(1), 39-45
10. Sashidhara, G.M.; Goudar, T.R. J. Indian Chem. Soc. 2001, 78, 360
11. Kalluraya, B.; Gururaya, R.; Ganesha Rai, Indian J. Chem, 2003, 42B, 211
12. Toyssie, P.; Charatte, J.J. Spectrochim, Acta 1963, 19, 1407
13. Srinnivas, B. ; Arulsamy, N. ; Zacharias, P.S. Polyhedron 1991, 10, 731
14. Gruber, S.J.; Harris, C.M.; Sinn, E.J. Inorganic Nucl. Chem. 1968, 30, 1805

15. Black, S.I.; Young, G.B. Polyhedron. 1989. 8(5), 555-596
16. Mohapatra, B. B.; Saraf, S. K. J. Indian Chem. Soc. 2003, 8, 696
17. Agarwal, R.K.; Singh, L. Turk. J. Chem, 2005, 309-316.
18. Wang, G.; Chang, J.C. Synth. React. Inorg. Met – Org. Chem. 1994, 24, 1091
19. Blake, A.B.; Cotton, F.A.; Octahedral and Tetrahedral complexes of Co(II). Inorganic Chemistry 1964, 3: 5 -6
20. Purell, K. F. and Kotz, J.C. Inorganic Chemistry, Holt-Saunders International Edn W.B. Saunders Company, Philadelphia London 1997 p.559-567
21. Sacconi, L. Electronic Structure and Stereochemistry of Ni(II) in Transition Metal Chemistry, 1968, Vol.4, p. 199-298.
22. Balhausen, C.J.; Gray, H.B. The Molecular Orbital Treatment of $[VO(H_2O)_5]^{2+}$. Inorganic Chemistry 1, 1962 p. 111-112
23. Ukwueze, A.C. Bull. Chem. Soc. Ethiop. 1993, 7(1), 61-66.

[1]Adedibu C. Tella* , [1]Wahab A. Osunniran , [1]Samson O. Owalude and [2]Ojeyemi M. Olabemiwo

[1]Department of Chemistry, P.M.B. 1515, University of Ilorin. Ilorin, Kwara State, Nigeria.

[2]Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, Nigeria