



Synthesis and Characterization of Fe(II) and Mn(II) Complexes of Schiff Base derived from Ninhydrin and L-Valine

¹Mekuanint Hika, ²Ponnusamy Thillai Arasu and ^{3*}Achalu Chimdi

¹Department of Chemistry, College of Natural and Computational Sciences, Enjibara University, Ethiopia

²Department of Chemistry, College of Natural and Computational Sciences, Wollega University, Post Box 395, Nekemte, Ethiopia, E.Mail: drpthillaiarasu@gmail.com

^{3*}College of Agriculture and Veterinary Sciences, Ambo University, P.O Box: 19, Ambo, Ethiopia, E-mail ID: achaluchimdi@yahoo.com

Abstract : The metal complexes of both Mn(II) and Fe(II) were synthesized using template synthesis method in ethanolic media. The metal complexes of Mn(II) and Fe(II) synthesized were colored complexes and stable to atmospheric conditions. The metal Mn(II) and Fe(II) complexes were soluble in common organic solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol and insoluble in methanol and water. Both complexes such as Mn(II) and Fe(II) were characterized by using elemental analysis, molar conductance, magnetic susceptibility, infrared spectroscopy and electronic spectral studies. The analytical data showed that the complexes having six coordination number with the following formulas $[MnL_2]$ and $[FeL_2]$ where L= Indane-1, 3-Dione-2-imine-N-3-methylbutanoate. The Schiff base L was shown to behave as a monobasic tridentate ONO donor. Results obtained from the magnetic susceptibility measurement of Schiff base complexes of Mn(II) and Fe(II) revealed that, the metal complexes have paramagnetic properties. From the values of conductivity measurement were 12.5 and 18.47 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for Mn(II) and Fe(II) respectively and they were non-electrolyte and coordinated with two ligands per metal ions (1:2) metal to ligand ratio. From the above data the geometry proposed for Mn(II) and Fe(II) complexes were octahedral geometry. All data obtained from FTIR, UV-VIS, elemental analysis, molar conductivity magnetic susceptibility confirmed that the formation of Schiff base (L) complexes of Mn(II) and Fe(II).

Key words : L-valine, Indane-1, 3-Dione-2-imine-N-3-methylbutanoate (IDIMB), Metal complexes, Schiff base.

Introduction

The chemistry and applications of Ninhydrin reactions with a variety of substrates has undergone and continue to undergo major developments over the course of nearly 100 years (Drochioiu et al., 2011). Ninhydrin (triketohydrindene hydrate) is a very useful colorimetric reagent for the identification and analysis of amino acids and its use has been extended to the paper chromatography of amino acids and protein hydrolyzates [1]. Ninhydrin reactions using manual and automated techniques as well as Ninhydrin spray reagents are widely used to analyze and characterize amino acids, peptides, and proteins as well as numerous other Ninhydrin-positive compounds in biomedical, clinical, food, forensic, histo-chemical, microbiological, nutritional, and plant studies [2].

Valine is essential amino acid widely distributed but rarely occurs in amount exceeding 10%. It is branched chain amino acid and can be derived from alanine by the introduction of two methyl group present on α -carbon atom. It forms methylmalonyl-CoA which can be converted to succinyl-CoA in place of two H atoms of the methyl group (Noori et al., 2012). Lack of L-valine may influence the growth of body, cause neuropathic obstacle and anemia [3].

Fe(III) with a d^5 configuration forms mostly octahedral complexes and comparatively less number of square planar complexes. It favors high spin complexes. The metal ion of Mn(II) forms many complexes in which the metal ion is octahedrally coordinated and most of them are high spin implying the absence of ligand field stabilization energy [4]. Meanwhile, iron is an essential trace element, and is the main component of hemoglobin in human blood, because the Fe (III) ion has the most self-spin single electrons, the design, synthesis, and characterization of iron complexes with Schiff base ligands play the vital role in coordination chemistry due to the importance as synthetic models for the functional materials [5]. Special attention has been paid to the studies of manganese complexes with ligands containing N and/or O donors, due to their interesting coordination chemistry and their role in inorganic biochemistry, catalysis and optical or magnetic materials [6].

Schiff bases are the compounds containing azomethine group ($-\text{HC}=\text{N}-$). They are condensation products of ketones or aldehydes with primary amines and were first reported by Hugo Schiff in 1864. Formation of Schiff base generally takes place under acid or base catalysis or with heat. The common Schiff bases are crystalline solids, which are feebly basic but at least some form insoluble salts with strong acids

This study was covered the synthesis, purity, solubility, melting point, molar conductivity measurements, magnetic susceptibility, elemental analysis, characterization of the metal complexes using spectroscopic studies (FTIR) of the complexes obtained during the reaction of ninhydrin with salts of Fe (II) and Mn (II) and L-valine.

Experimental Techniques and Instrumentation

Chemicals

All chemicals used in this study were analytical grade. Ninhydrin (95%), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were purchased from Micron International Trading House PLC. L-Valine was purchased from Ranchem Industry and Trading. Ethanol was used as the solvent for synthesis were purchased from Neway PLC. Other reagents such as AgNO_3 used for chloride test and chloroform, hexane, diethyl ether, petroleum ether those were used for solubility test and distilled water which was used as a solvents in the investigation were Analytical grade.

Instrumentation

Melting/decomposition temperatures were determined with digital melting point apparatus. The purity of the complex and ligand were checked by thin layer chromatography (TLC). Molar conductivity of the complexes was measured at room temperature with freshly prepared solution in DMF using conductivity meter. Magnetic susceptibility measurement of the complex was recorded at 21°C on MSB-AUTO Sherwood Scientific Ltd. Magnetic Susceptibility balance. The FTIR was recorded using Thermo Fischer FT-IR spectrometer in the range of 550-4000 cm^{-1} . The amount of light absorbed by a sample at each wavelength of the UV and visible regions of the electromagnetic spectrum is measured by a UV-VIS run using Lambda 950

UV/VIS/NIR/ spectrometer. The elemental analysis of the complexes were run with EA 1112 Flash CHNS/O-analyzer.

Synthesis of Metal [Mn(II) and Fe(II)] Complexes using Ninhydrin and L-valine

The transition metal complexes of the metals Mn(II) and Fe(II) were synthesized using a general procedure. A 0.005 Mole of ninhydrin (0.89 gram) was dissolved in minimum possible amount of absolute ethanol (~12 -15 mL) similarly, 0.005 mole of the metal salt (MnCl₂.4H₂O and FeCl₂.4H₂O) was dissolved in the minimum possible amount of absolute ethanol; and the two solutions were mixed together. And the mixture was refluxed for 45 minutes. 0.005 mole of L-valine (0.58 gram) was dissolved in a 50:50 mixture of absolute ethanol and distilled water (~ 14 mL of each) and added to the above solution while refluxing.

The mixture was refluxed for other additional two hours. The resulting colored precipitate was then filtered off while hot and washed first with distilled water and then with absolute ethanol. The product was then left in open air for drying, weighed and stored in desiccators until it was dried.

Results and Discussions

General

Physical properties, purity, solubility, elemental analysis, molar conductance, electronic spectral and magnetic susceptibility of the complexes discussed in the following sections

Physical Characteristics of the Complexes

Both complexes were powders and do not melt/ decompose up to 472 °C which have also low yields. The yield of manganese complex is 16.217 % and the yield of iron complex is 15.752 %. Their physical characteristics are shown here in Table 1. Both complexes are colored. Manganese complex have dark violet color and iron complex was green colored.

Table 1: Physical characteristics of the complexes

S.No	Complex	Color	Appearance	Yield (%)	Mp (D T) °C
1	FeL ₂	Green	Powder	15.752	>472
2	MnL ₂	Dark violet	Powder	16.217	>472

Where: L is C₁₄N₄H₁₂

The metal complexes of both Mn(II) and Fe(II) were subjected to the solubility test and they are soluble in common organic solvents which have high dielectric constant such as: DMF, DMSO, ethanol and they are insoluble in methanol and water as shown in Table 2.

Table 2: The solubility of the compounds in some common organic solvents

S.No	Complex	Solvents				
		DMF	DMSO	Ethanol	Methanol	Water
1	FeL ₂	S	S	S	IS	IS
2	MnL ₂	S	S	S	IS	IS

Where: S stands for soluble and IS stands for insoluble

Analytical and Molar Conductance Studies

The absence of chloride ion in the product has been chemically verified. The composition of the complexes matches satisfactorily with the presence of ethanol in each complex (Kebede et al., 2006). The analytical data matches with 1:2 metal to Schiff base complexes of Mn(II) and Fe(II). The elemental analysis data of the complexes are given in Table 5. The analytical data matches (though carbon value deviates) hydrogen and nitrogen analysis are in good match with the proposed compositions with 1:2 metals to Schiff base complexes in an octahedral geometry for the complexes of Mn(II) and Fe(II). The specific conductance (Sc) of 0.0116M solution of the complexes at 25 °C is 31 μS for Fe(II) and 21 μS for Mn(II) and the molar conductance

calculated, Λ_M , is $12.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for Mn(II) and $18.47 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for Fe(II). Comparison of a molar conductance of the complexes with the known range in DMF, the following Table 3 helps to correlate the conductivity nature of the complexes. Expected molar conductance (Λ_m) range for 2,3,4, and 5 ion electrolytes ($\approx 10^{-3} \text{ M}$) in DMF at 25°C [7].

Table 3: Molar conductance vs. number of ions in DMF

S.No	Number of ions	Λ_m (S $\text{cm}^2 \text{mol}^{-1}$)	Electrolyte type
1	None	<65	Non- electrolyte
2	2	65-90	1:1
3	3	130-170	2:1
4	4	200-240	3:1
5	5	-	4:1

Thus for the above conductance values of the complexes is summarized in table 4 below:

Table 4: Molar Conductivity of the metal complexes in DMF

S.No	Complex	Solvent	$\Lambda_{M \text{ DMF}}$ $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	Type of Electrolyte
1	MnL ₂	DMF	12.5	Non-electrolyte
2	FeL ₂	DMF	18.47	Non-electrolyte

The conductance values of the complexes obtained from instrumental values were converted into molar conductance which is very small which were in the range of $10\text{-}20 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ this shows that the complexes are non-electrolytes [8].

Table 5: Analytical data for metal complexes of Schiff base ligand

S.No	Complex	% N found (cal.)	% C found (cal.)	% H found (cal.)
1	MnL ₂	3.96 (4.92)	65.61 (59.05)	3.16 (3.87)
2	FeL ₂	3.89 (4.91)	66.82 (58.94)	2.62 (3.86)

Where: L is C₁₄NO₄H₁₂ and cal is calculated value

Infrared Spectral Data

The Infrared data are given in Table 6. From the data the sharp NH stretching band of the free amino acids at $3000 - 2900 \text{ cm}^{-1}$ and a broad band in the region of $3300\text{-}3100 \text{ cm}^{-1}$ is due to ν_{OH} stretching and two characteristic bands in the region $1748\text{-}1710 \text{ cm}^{-1}$ are due to $\nu_{\text{C=O}}$ the stretching frequency of Ninhydrin and L-valine were not observed in the complex spectra, indicating the derivatization of the Schiff base and the disappearance of the functional group of the amino acid and Ninhydrin [9]. It shows three bands in the C=O stretching 1760 , 1747 and 1710 cm^{-1} 1747 and 1710 are the characteristic bands of 1,3- dicarbonyl functional group and 1760 is the intermediate carbonyl in the tricarbonyl species which is in equilibrium with dihydroxy species. But in the product there are two carbonyls stretching frequency the intermediate carbonyl one is not shown that indicates the derivatization of the Schiff base. Both complexes show two strong bands in the carbonyl stretching region, that is the characteristics of 1,3-dicarbonyl functional group.

Table 6: IR spectral data of the metal complexes and the starting material

S. No	Compounds	ν OH/NH	ν C=O free	ν C=O coordination	ν C=C aromatic	ν C=N	ν_a CO O ⁻	ν_s CO O ⁻	ν O-C	ν M-X
1	Ninhydrin	3300-3086	1760 1747 1710	-----	1600	----- -	----- -	----- -	----- -	-----
2	L-valine	2936	-----	-----	-----	----- -	1608	1394	----- -	-----
3	FeL ₂	-----	1715 (m)	1700 (m)	1590 (m)	1540	1630	1310	1290 (vs)	715 599
4	MnL ₂	----- -	1720 (s)	1705	1580 (s)	1500 (vs)	1630 (s)	1345	1305 (w)	700 (s) 590(m)

Where: ν - represents stretching, δ - bending or deformation, s- for strong, vs- for very strong, m- for medium, w- for weak, a- for asymmetric, s- for symmetric, arom- aromatic, X is oxygen or nitrogen while M is the metal ion and L is the Schiff base of Ninhydrin and L-valine (C₁₄NO₄H₁₂)

There is the decrement of (532 cm⁻¹) that indicates one carbonyl in coordination. The disappearance of 1760 cm⁻¹ carbonyl stretching band of Ninhydrin and the loss of NH stretching bands of the amino acid (L-valine) shows the condensation reaction of these two functional groups and forms the Schiff base. L-valine and free amino acids show strong carboxyl anti symmetric stretching peak at 1600-1590 cm⁻¹ and a weaker symmetric stretching at ~1400cm⁻¹[9].

In the complexes the symmetric stretching peak appears in between 1300-1350 cm⁻¹, while the anti-symmetric stretching mode appears in the range of 1665-1630 cm⁻¹. The positive shifts of anti-symmetric stretching peak and the negative shift of symmetric stretching peak is the evidence for the coordination through the ionized carboxyl group via oxygen. The separation between the frequencies vary with metal ions involved and the observed pattern is agrees with reports [9].

The complex of Fe(II)also shows a new, strong and sharp peak at 1540 cm⁻¹, which indicates the presence of a coordinated azomethine group. And shows medium peak around 1700cm⁻¹ that is for the coordinated carbonyl stretching frequency and around 1590 cm⁻¹ there was medium peak for aromatic carbons. The asymmetric stretching of the carboxyl was found at 1630 cm⁻¹ around 1310 cm⁻¹ there was the stretching of symmetric stretching. The Fe(II) complex shows very sharp O-C stretching at 1290 cm⁻¹.The complex of Mn(II) shows strong and sharp band at 1720 cm⁻¹ which for the coordinated azomethine group formed from the condensation of ninhydrin and L-valine. At 1705 cm⁻¹ there was medium peaks of coordinated carbonyl group, at 1580 cm⁻¹ there was peak for aromatic carbons. The asymmetric stretching of the carboxyl was found at 1630 cm⁻¹ and around 1345 cm⁻¹ there was the symmetric stretching. The Mn(II) complex shows very sharp O-C stretching at 1305 cm⁻¹.

In the presence of transition metal ions Mn(II) and Fe(II) thereaction does not lead to the formation of Ruhmann's purple but stops at the firstcondensation step and forming a stable Indane-1, 3-dione-2- imine-N-3- methylbutanoate (IDIMB), the ketimine, which act as a tridentate (ONO) donor ligand. Generally the FTIR data shows that the Schiff base coordinated via oxygen of carbonyl and nitrogen of the azomethine in both Mn(II) and Fe(II) complexes. The uncoordinated carbonyl stretching frequency occurs at 1720. Here the decreasing frequency indicates the coordination of carbonyl with metal ions. The uncoordinated carbonyl of the complexes shows weak stretching frequency around 1710- 1730. And the complexes show M-N and M-O stretching frequency between 580-720. Comparing with Ninhydrin, in the spectrum of this complex only two carbonyl stretching peaks at a decreased wave numbers (1720 – 1700 cm⁻¹) are found, which shows the derivatization of the higher frequency (1760cm⁻¹)carbonyl group in ninhydrin [9]. The above IR data analysis is consistent with the complexation of the Schiff base (ketimine).

Magnetic susceptibility and electronic spectral studies

The magnetic susceptibility and electronic spectral data of the metal complexes are given in Table 7. The electronic spectroscopy was measured in ethanol. Ninhydrin and L-valine form a deep blue/purple colored compound known as the Ruhmann's purple, which maximally absorbs at 412nm and 571nm. This azomethine band of the Ruhmann's purple because is very strong, is thought to obscure some d-d bands of the complexes in the region. The electronic spectral data of the metal complexes are given in Table 7. The bands observed at 256nm and 285nm in the complexes are assigned to the $\pi \rightarrow \pi^*$ transition of the benzene moiety [4]. A very strong band near 500nm is assigned to a combination of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the azomethine chromophores which in the Free State absorbs between 400 – 429.9nm. The observed bathochromic shift gives strong support for the coordination of the azomethine nitrogen [10].

The magnetic susceptibility measurement was measured at 21 °C. The results calculated from instrumental reading in gram susceptibility changed into effective magnetic moment that is for manganese complex 1.6896 Bm and for iron complex have effective magnetic moment of 2.797 Bm showed that the metal complexes were paramagnetic and it can be observed that all the complexes prefer a low spin configuration, which is exhibited due to the presence of strong field ligands, such as the azomethine and carbonyl groups. Such bands of the coordinated azomethine group are also observed at 443nm in the Mn (II) complex and at 489nm in the Fe (II) complexes,[11] which indicate the presence and coordination of the azomethine group. These are assigned to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the azomethine chromophore. The Mn(II) complex show a number of very weak d-d bands, consistent with a high spin d^5 octahedral system. ${}^6A_{1g} \rightarrow {}^4E_g$ (D), ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (P), ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (D) and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G). The transitions are observed around 300nm, 334nm, 348nm and 392nm respectively. And Fe(II) complex show very weak d-d bands, consistent with a high spin d^6 octahedral system. ${}^6A_{1g} \rightarrow {}^4E_g$ (G), ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^6A_{1g} \rightarrow {}^4E_g$ (D), ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (D), ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G). The transitions are observed around 390nm, 494nm, 517nm and 363nm.[12].

Table 7: Electronic spectral data of MnL_2 and FeL_2 , assignment and Magnetic moment values

S.No	Complex	Non ligand electronic spectral bands (nm)	Assignment	μ_{eff} (BM)
1	MnL_2	300, 334, 348 and 392	${}^6A_{1g} \rightarrow {}^4E_g$ (D), ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (P), ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (D) and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G)	1.6896
2	FeL_2	390, 494, 517 and 363	${}^6A_{1g} \rightarrow {}^4E_g$ (G), ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^6A_{1g} \rightarrow {}^4E_g$ (D), ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (D), ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G)	2.797
3	R	247	The bands of uncoordinated azomethine transition	=====

Based on the obtained data from the FTIR, electronic spectra, magnetic susceptibility, molar conductance measurements the structure and the geometry proposed for the reaction between L- valine and ninhydrin in the presence of some of Mn(II) and Fe(II) were octahedral as shown on the Figure 1 below.

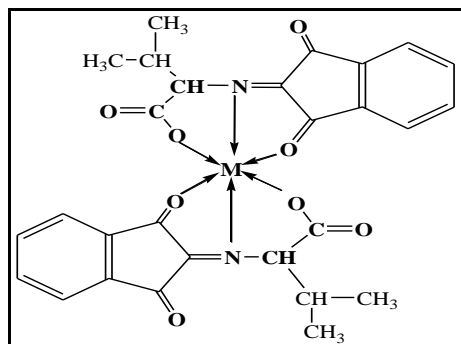


Figure 1: The proposed structure of metal complex of Schiff base $[ML_2]$, M = Mn and Fe

Conclusion

Ninhydrin and L-valine undergo a condensation reaction to give Schiff base, indane-1,3-dione-2-imine-N-2-(3-methylebuthionate), IDIMB that forms colored complexes with Mn(II) and Fe(II) by the template synthesis. The Schiff base ligand behaves as a monobasic tridentate ONO donor which forms two five membered ring on complexing with Mn(II) and Fe(II). The MnL_2 and FeL_2 complexes were soluble in common organic solvents such as DMF, DMSO, ethanol and insoluble in methanol and water. From the magnetic susceptibility measurements the effective magnetic moment of Mn(II) complex was 1.6896 BM this showed Mn(II) complex have paramagnetic properties and the effective magnetic moment of Fe(II) complex was 2.797 BM this also showed that Fe(II) complex have paramagnetic properties. From the conductivity measurement the molar conductance calculated from the specific conductance of the MnL_2 and FeL_2 complexes which have 12.5 and 18.47 BM molar conductance value of MnL_2 and FeL_2 respectively that shows both complexes have non-electrolytic properties. Thus, based on the analytical, molar conductance, IR spectra, electronic spectra and magnetic susceptibility data assured the formation of the Schiff base (IDIMB) metal [Mn(II) and Fe(II)] complexes and from those data the geometry both complexes proposed to be octahedral structure.

Acknowledgement

The authors would like to thanks the Wollega University for the laboratory facility support and Mekuanint Hika also thanks to Ministry of Science and Higher Education of Ethiopia for sponsoring to pursue the program.

References:

1. Alejandro Dominguez Xorge The preparation of ninhydrin as a laboratory experiment J. Chem. Educ. 1953, 30, 12, 624
2. Friedman, Applications of the Ninhydrin Reaction for Analysis of Amino Acids, Peptides, and Proteins to Agricultural and Biomedical Sciences. Journal of Agricultural and Food chemistry, 2004, 52, 385–406
3. Bhushanavathia and Rao. Speciation studies of Co(II), Ni(II) and Cu(II) complexes of L-valine in acetonitrile–water mixtures. Chemical Speciation and Bioavailability, 2013, 25(4), 258-264.
4. Getachew. Studies on First Row Transition Metal Complexes Derived From Ninhydrin and Amino Acids Having Polar (Threonine) and Nonpolar (Leucine) Side Chains. MSc Thesis, AAU, chemistry. 2003.
5. Feng . A Binuclear Iron(III) Schiff Base Complex Doubly Bridged by Hydroxyl Groups: Synthesis, Structure, and Characterization. Russian Journal of Coordination Chemistry, 2015, 41(2), 101-107.
6. Bartyzel and Kaczor. The formation of a neutral manganese(III) complex containing a tetradentate Schiff base and a ketone–synthesis and characterization. Journal of Coordination Chemistry, 2015. 1-17
7. Berhanu. . Template Synthesis And Characterization Of Ni(Ii) And Zn(Ii) Complexes Derived From Ninhydrin And Ethylenediamine. MSc Thesis, AAU 2009
8. Goel , Schiff's Base Ligands and Their Transition Metal Complexes as Antimicrobial Agents. Journal of Chemical, Biological and Physical Sciences, 2014 (3), 1946-1964
9. Nakamoto. (1997). Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry. A John Wiley & Sons, Inc., Publication 1997
10. Raju et al. (2011). Synthesis, spectral characterization, catalytic and biological studies of new Ru(II) carbonyl Schiff base complexes of active amines. Natural Science, 3(7), 542-550
11. Kebede , Synthesis and characterization of 2,4,6-tris(hydrazino)-s-triazine and its metal complexes. Transition Metal Chemistry, 2006,31, 19–26
12. Noori , Synthesis, Characterization, And Antibacterial Activities Of Manganese (II), Cob alt(II), Iron (II), Nickel (II) , zinc (II) And Cadmium(II) Mixed Ligand Complexes Containing Amino Acid(L-Valine) And Saccharin. Advances in Physics Theories and Applications, 2012, 9, 1-13
