



Faculty of Sciences

M.Sc. Thesis In Inorganic Chemistry

**Synthesis of a Nano Uranyl Schiff base Complex and
Synthesis, Characterization and Kinetic Studies of Uranyl
Saloph-type Schiff base Complexes**

By

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September 2012

In The Name of God

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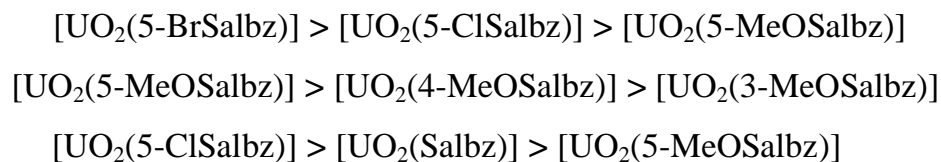
ABSTRACT

Synthesis of a Nano Uranyl Schiff base Complex and Synthesis, Characterization and Kinetic Studies of Uranyl Saloph-type Schiff base Complexes

By

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In this thesis some tetradentate N_2O_2 Schiff base ligands are prepared by the condensation reaction between 2-aminobenzylamin with salicylaldehyde and its derivatives (5-Cl, 5-Br, 5-OMe, 4-OMe, 3-OMe, 5-H) and so on in MeOH (2:1 mol stiochiometric ratio). Also all Schiff base complexes are synthesized in MeOH (1:1 mol stiochiometric ratio of Schiff base and uranyl acetate). Schiff bases and their complexes are characterized by 1H NMR, IR and C.H.N. analyses. Some complexes are characterized by TG studies and one of them is characterized by X-ray crystallography. Also we synthesized the nano structure of $[UO_2(5-BrSalbz)(MeOH)]$ complex. Kinetic studies are performed for thermal decomposition and also spectrophotometrically for the reaction between tributylphosphines as donor with the uranyl Schiff base complexes as acceptor. Rate reaction of PBu_3 with the complexes shows the trend below:



Biological activity of some of these complexes were studied, and it showed that $[UO_2(5-ClSalbz)(MeOH)]$ has anti cancer activity.

The electrochemical properties of U(VI) complexes were studied. The cyclic voltammograms of uranyl complexes all exhibit a reversible redox process which is most likely due to the $[UO_2]^{2+}/[UO_2]^+$ couple.

LIST OF TABLES	XI
LIST OF FIGURES	XII
LIST OF SCHEME	XVII
ABBREVIATION	XVIII

CHAPTER ONE

	PAGE
INTRODUCTION	2
1.1. Schiff base	2
1.2. Quinonimines/quinone imines	5
1.3. Nomenclature and classification.....	6
1.4. Aldimines and ketimines.....	7
1.5. Schiff bases and their metal complexes.....	8
1.6. General aspects of Salen complexes.....	10
1.7. Structural Aspects of Metallo-Salen Complexes.....	12
1.8. Uranyl Schiff base complexes.....	14
1.9. Uranyl and its property chemistry.....	15
1.10. Thermogravimetric analysis and it's kinetic studies.....	16
1.11. Nano schiff base complexe.....	17
1.12. The Objective of This Project.....	18

CHAPTER TWO

EXPERIMENTAL	19
2.1 Chemicals	20
2.2. Instruments	20
2.3. Synthesis and Characterization of Compounds	21
2.3.1. The synthesis of unsymmetrical Schiff base ligands.....	21
2.3.2. The synthesis of uranyl Schiff base complexes [UO ₂ (Schiffbase) (MeOH)].....	24
2.3.3. Synthesis of nano uranyl Schiff base complexe.....	28
2.3.4. The synthesis of kinetic product, [UO ₂ (Schiff base)(PBU ₃).....	29
2.4. Crystal growth for X-ray crystallography.....	29
2.7. Cyclic voltammetry	30
2.6. Kinetic studies.....	30

CHAPTER THREE

RESULTS AND DISCUSSION	32
3.1. General considerations	33
3.2. Identification of compounds	33
3.2.1. IR Spectra.....	33
3.2.2. ¹ H NMR Spectra	36
3.2.3. Elemental microanalysis	39
3.2.4. UV-vis spectra	39

3.3. Kinetic studies.....	42
3.3.1. Result and discussion.....	44
3.3.2. Comparing 5-Br, 5-Cl and 5-MeO complexes.....	44
3.3.3. Comparing 3-MeO, 4-MeO, 5-MeO complexes.....	44
3.3.4. Temperature effect.....	45
3.4. X-ray crystallography	47
3.4.1. X-ray crystal structure determination.....	47
3.4.2. Crystal structure determination of the complex and packing structure.....	48
3.5. Thermal analysis (TGA).....	52
3.5.1. Kinetic aspects of TG.....	54
3.6. Anti cancer activity.....	56
3.6.1. Cell culture and MTT assay for analysis of anticancer properties of complexes.....	56
3.7. Cyclic voltametry.....	59
Appendix.....	61
References.....	87

LIST OF TABLES

TABLE	PAGE
3.1. The infrared frequencies of the Schiff bases and their complexes(cm^{-1})...	35
3.2. ^1H NMR spectrum (δ , ppm) in $\text{DMSO}-d_6$ or CDCl_3 solvent of the Schiff bases and complexes.....	38
3.3. UV-Vis bands of the Schiff bases in $\lambda_{\text{max}}(\text{CH}_3\text{CN}/\text{nm})$	41
3.4. UV-Vis bands of the uranyl Schiff base complexes in $\lambda_{\text{max}}(\text{CH}_3\text{CN}/\text{nm})$	41
3.5. Pseudo-first-order rate constant $10^2\text{K}_2(\text{M}^{-1}\text{s}^{-1})$ for the reaction of $[\text{UO}_2(\text{Salbz})(\text{CH}_3\text{CN})]$ with PBu_3 at different temperature.....	45
3.6. values of the activation parameters ΔH^\ddagger , ΔG^\ddagger and ΔS^\ddagger for the interaction of the complexes with PBu_3	47
3.7. Crystal data, data collection and structure refinement details for complex $[\text{UO}_2(3\text{-MeOSalbz})(\text{DMF})]$	48
3.8. Selected bond distances (\AA) and angles ($^\circ$) for complex $[\text{UO}_2(3\text{-MeOSalbz})(\text{DMF})]$	49
3.9. The results of thermal decomposition of uranyl Schiff base complexes...	53
3.10. Thermal and kinetic parameters for uranyl complexes.....	55
3.11. The IC_{50} values (Mm/ml) of the complexes against Jurkat cell line.....	57
3.12. Redox potential data of uranyl Schiff base complexes in acetonitrile solution.....	60
3.13. Pseudo-first-order rate constant $10^2\text{K}_2(\text{M}^{-1}\text{s}^{-1})$ for the reaction of $[\text{UO}_2(3\text{-MeOSalbz})(\text{CH}_3\text{CN})]$ with PBu_3 at different temperature.....	78
3.14. Pseudo-first-order rate constant $10^2\text{K}_2(\text{M}^{-1}\text{s}^{-1})$ for the reaction of $[\text{UO}_2(5\text{-MeOSalbz})(\text{CH}_3\text{CN})]$ with PBu_3 at different temperature.....	80

3.15. Pseudo-first-order rate constant $10^2K_2(M^{-1}s^{-1})$ for the reaction of $[UO_2(4-MeOSalbz)(CH_3CN)]$ with PBu_3 at different temperature.....	80
3.16. Pseudo-first-order rate constant $10^2K_2(M^{-1}s^{-1})$ for the reaction of $[UO_2(5-BrSalbz)(CH_3CN)]$ with PBu_3 at different temperature.....	81
3.17. Pseudo-first-order rate constant $10^2K_2(M^{-1}s^{-1})$ for the reaction of $[UO_2(5-ClSalbz)(CH_3CN)]$ with PBu_3 at different temperature.....	81
3.18. Analytical data of the kinetic product, $[UO_2(5-BrSalbz)(PBu_3)]$ complex.....	81

LIST OF FIGURES

FIGURES	PAGE
1.1. General structure of a Schiff base. R^1 , R^2 , and/or R^3 = alkyl or aryl.....	2
1.2. Examples of bioactive Schiff bases.....	3
1.3. Reaction between a carbonyl compound with an amine (Schiff base formation).....	3
1.4. Structure of o-benzoquinone diimine	5
1.5. The structure of salen-type Schiff bases and their abbreviations (a,b,c).....	6
1.6. Classification of multidentate Schiff base ligands	7
1.7. General structure of a aldimine and ketimine.....	8
1.8. The four most common coordination modes of the Salen complexes: a) Square-planar, b) Square pyramidal, c) octahedral, d) Pentagonal-bipyramidal and L= neutral or charged ligand.....	13

1.9. Schematic drawing of a = <i>cis</i> - β - and b = <i>cis</i> - α -folded conformations. L=charged or neutral ligand or vacant site.....	14
1.10. Example of Uranyl Schiff base complexes.....	15
1.11. Uranium rock.....	15
1.12. Aqueous solutions of uranium III, IV, V, VI salts respectively from left	16
2.1. TEM image of nano-particle.....	28
2.2. View of the single crystal of [UO ₂ (3-MeOSalbz)(DMF)] complex.....	30
2.3. UV–vis spectral changes of [UO ₂ (3-MeOSalbz)(MeOH)] (2.4×10 ⁻⁴ M) with excess [PBU ₃] in CH ₃ CN.....	31
3.1. IR spectrum of H ₂ (4-MeOSalbz).....	33
3.2. IR spectrum of [UO ₂ (4-MeOSalbz)(MeOH)] complex.....	35
3.3. ¹ H NMR spectrum of H ₂ Salbz in CDCl ₃	37
3.4. ¹ H NMR spectrum of [UO ₂ (Salbz)(MeOH)] in DMSO.....	37
3.5. The electronic spectra of H ₂ Salbz and [UO ₂ (Salbz)(MeOH)] in CH ₃ CN at room temperature.....	40
3.6. UV–vis spectral changes for [UO ₂ (3-MeOSalbz)(MeOH)] (2.4×10 ⁻⁴ M) with excess [PBU ₃] in CH ₃ CN.....	42
3.7. The plots of k _{obs} vs. [PBU ₃] for [UO ₂ (Salbz)(CH ₃ CN)] at different temperatures (10 - 40°C).....	43
3.8. The linear plot for ln(k ₂ /T) against 1/T for [UO ₂ (Salbz)(CH ₃ CN)].....	46
3.9. The X-ray crystal structure of complex [UO ₂ (3-MeOSalbz)(DMF)] complex.....	49
3.10. Packing diagram of [UO ₂ (3-MeOSalbz)(DMF)] complex.....	51
3.11. Hydrogen-bonding in the structure of [UO ₂ (3-MeOSalbz) (DMF)]	

complex.....	51
3.12. The viability(%) vs. complex concentration.....	58
3.13. The viability(%) vs. complex concentration....	58
3.14. Cyclic voltammograms of [UO ₂ (Salbz)(MeOH)], in acetonitrile at room temperature. Scan rate: 0.1 V/s.....	60
3.15. The plots of k_{obs} vs. [PBu ₃] for [UO ₂ (3-MeOSalbz)(MeOH)] at different temperatures (10-40°C).....	62
3.16. The plots of k_{obs} vs. [PBu ₃] for [UO ₂ (5-BrSalbz)(MeOH)] at different temperatures (10-40°C).....	62
3.17. The plots of k_{obs} vs. [PBu ₃] for [UO ₂ (5-ClSalbz)(MeOH)] at different temperatures (10-40°C).....	63
3.18. The plots of k_{obs} vs. [PBu ₃] for [UO ₂ (Salbz)(MeOH)] at different temperatures (10-40°C).....	63
3.19. The plots of k_{obs} vs. [PBu ₃] for [UO ₂ (4-MeOSalbz)(MeOH)] at different temperatures (10-40°C).....	64
3.20. The linear plot for $\ln(k_2/T)$ against $1/T$ for [UO ₂ (3-MeOSalbz)(MeOH)].....	64
3.21. The linear plot for $\ln(k_2/T)$ against $1/T$ for [UO ₂ (5-MeOSalbz)(MeOH)].....	65
3.22. The linear plot for $\ln(k_2/T)$ against $1/T$ for [UO ₂ (5-BrSalbz) (MeOH)]	65
3.23. The linear plot for $\ln(k_2/T)$ against $1/T$ for [UO ₂ (5-ClSalbz) (MeOH)]	66
3.24. The linear plot for $\ln(k_2/T)$ against $1/T$ for [UO ₂ (Salbz) (MeOH)].....	66
3.25. The linear plot for $\ln(k_2/T)$ against $1/T$ for [UO ₂ (4-MeOSalbz)(MeOH)].....	67

3.26. IR spectrum of H ₂ (Salbz).....	68
3.27. IR spectrum of [UO ₂ (Salbz)(MeOH)] complex.....	68
3.28. IR spectrum of H ₂ (5-MeOSalbz).....	69
3.29. IR spectrum of [UO ₂ (5-MeOSalbz)(MeOH)].....	69
3.30. IR spectrum of H ₂ (3-MeOSalbz).....	70
3.31. IR spectrum of [UO ₂ (3-MeOSalbz)(MeOH)] complex.....	70
3.32. IR spectrum of H ₂ (5-ClSalbz).....	71
3.33. IR spectrum of [UO ₂ (5-ClSalbz)(MeOH)] complex.....	71
3.34. IR spectrum of H ₂ (5-BrSalbz).....	72
3.35. IR spectrum of [UO ₂ (5-BrSalbz)(MeOH)] complex.....	72
3.36. IR spectrum of kinetical product, [UO ₂ (5-BrSalbz)(PBu ₃)] complex....	73
3.37. ¹ H NMR spectrum of H ₂ (5-MeOSalbz) in CDCl ₃	74
3.38. ¹ H NMR spectrum of [UO ₂ (5-MeOSalbz)] in DMSO.....	74
3.39. ¹ H NMR spectrum of H ₂ (4-MeOSalbz) in CDCl ₃	75
3.40. ¹ H NMR spectrum of [UO ₂ (4-MeOSalbz)(MeOH)] in CDCl ₃	75
3.41. ¹ H NMR spectrum of H ₂ (3-MeOSalbz) in CDCl ₃	76
3.42. ¹ H NMR spectrum of [UO ₂ (4-MeOSalbz)(MeOH)] in CDCl ₃	76
3.43. ¹ H NMR spectrum of H ₂ (5-ClSalbz) in CDCl ₃	77
3.44. ¹ H NMR spectrum of [UO ₂ (5-ClSalbz)(MeOH)] in CDCl ₃	77
3.45. ¹ H NMR spectrum of H ₂ (5-BrSalbz) in DMSO.....	78
XII	
3.46. ¹ H NMR spectrum of [UO ₂ (5-BrSalbz)(MeOH)] in DMSO.....	78
3.47. ¹ H NMR spectra of kinetic product, [UO ₂ (5-BrSalbz) (PBu ₃)], in DMSO.....	

	79
3.48. TGA – DrTGA curves of [UO ₂ (3-MeOSalbz)(MeOH)].....	82
3.49. TGA–DrTGA curves of [UO ₂ (salbz)(MeOH)].....	82
3.50. TGA–DrTGA curves of [UO ₂ (4-OMesalbz)(MeOH)].....	83
3.51. TGA–DrTGA curves of [UO ₂ (5-Brsalbz)(MeOH)].....	83
3.52. TGA – DrTGA curves of [UO ₂ (5-BrSalbz)(CH ₃ CN)].....	84
3.53. Cyclic voltammogram of [UO ₂ (5-MeOSalbz)(MeOH)], in acetonitrile at room temperature. Scan rate: 0.1 V/s.....	84
3.54. Cyclic voltammogram of [UO ₂ (3-MeOSalbz)(MeOH)], in acetonitrile at room temperature. Scan rate: 0.1 V/s.....	85
3.55. Cyclic voltammogram of [UO ₂ (4-MeOSalbz)(MeOH)], in acetonitrile at room temperature. Scan rate: 0.1 V/s.....	85
3.56. Cyclic voltammogram of [UO ₂ (5-BrSalbz)(MeOH)], in acetonitrile at room temperature. Scan rate: 0.1 V/s.....	86
3.57. Cyclic voltammogram of [UO ₂ (5-ClSalbz)(MeOH)], in acetonitrile at room temperature. Scan rate: 0.1 V/s.....	86

LIST OF SCHEMES

SCHEME	PAGE
1.1. Formation mechanism of a Schiff base (a,b).....	4
1.2. Decomposition reaction of Schiff base.....	5
1.3. General methods of preparation of Schiff base complexes.....	12
2.1. Preparation of Schiff base.....	21
2.2. Preparation of the uranyl complexes.....	25
2.3. Preparation of single crystals of [UO ₂ (3-MeOSalbz)(DMF)] complex....	30

LIST OF ABBREVIATION

Definition	Abbreviation
δ	chemical shift
A	ampere
ε	extinction coefficient ($M^{-1}cm^{-1}$)
λ	wavelength
$^{\circ}C$	degree Celsius
Ar	aromatic
Calc	calculated
$CDCl_3$	deuterated chloroform
cm^{-1}	wavenumber
DMF	N,N'-Dimethylformamide
$DMSO-d_6$	deuterated dimethylsulfoxide
en	ethylenediamine
et al.	and others
g	gram
h	hour
H_2salbz	N,N'-bis(salicylidene)-2-aminobenzylamin
3-MeOsalbz	N,N'-bis(3-methoxysalicylidene)-2-aminobenzylamin
4-MeOsalbz	N,N'-bis(4-methoxysalicylidene)-2-aminobenzylamin
5-MeOsalbz	N,N'-bis(5-methoxysalicylidene)-2-aminobenzylamin
5-Brsalbz	N,N'-bis(5-bromosalicylidene)-2-aminobenzylamin
5-Clsalbz	N,N'-bis(5-chlorosalicylidene)-2-aminobenzylamin
Hz	Hertz (one cycle per second)

IR	infrared
M	molar, moles per litre (mol^{-1})
MHz	10^6 Hertz
Me	methyl
MeOH	methanol
salen	N,N'-bis(salicylaldehyde) ethylenediamine
min	minute
ml	millilitre (10^{-3} L)
mmol	10^{-3} mol
nm	nanometer (10^{-9} m)
NMR	nuclear magnetic resonance
OAc	acetate
PBu ₃	tributylphosphine
ppm	parts per million
Ph	phenyl
T	temperature
UV	ultraviolet
vis	visible
TBAP	tetrabutylammoniumperchlorate
IL	intra-ligand
TMS	Tetramethylsilane

CHAPTER ONE

1. Introduction

1.1 Schiff base

Schiff base ligands played an integral and important role in the development of coordination chemistry.^[1] The first preparation of imines was reported in the 19th century by Hugo Schiff (26 April 1834)(a German chemist).^[2,3,4,5] He discovered Schiff bases and other imines, and was responsible for research into aldehydes and had the Schiff test named after him. He also worked in the field of amino acids and the Biuret reagent . Since then a variety of methods for the synthesis of imines have been described.^[6] Schiff bases are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) (Fig. 1.1) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group(imine is used as a suffix in systematic nomenclature to denote the C=NH group excluding the carbon).

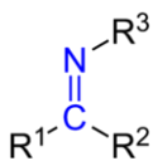


Fig. 1.1. General structure of a Schiff base. R¹, R², and/or R³ = alkyl or aryl

Schiff bases are some of the most widely used organic and inorganic compounds. Imine or azomethine groups are present in various natural, natural-derived, and non-natural compounds (see Fig. 1.2 for some examples). The imine group present in such compounds has been shown to be critical to their biological activities.^[7]