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

IN THE NAME OF GOD

Declaration

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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

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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 salicilaldehyde 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 ^{1}HNMR, 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 $[UO_2(5\text{-BrSalbz})(MeOH)]$ complex.Kinetic studies are performed for thermal decomposition and also spectrophotometrically for the reaction between tirbutylphosphins as donor with the uranyl Schiff base complexes as acceptor. Rate reaction of PBu_3 with the complexes shows the trend below:

$$[UO_2(5\text{-BrSalbz})] > [UO_2(5\text{-ClSalbz})] > [UO_2(5\text{-MeOSalbz})]$$

$$[UO_2(5\text{-MeOSalbz})] > [UO_2(4\text{-MeOSalbz})] > [UO_2(3\text{-MeOSalbz})]$$

$$[UO_2(5\text{-ClSalbz})] > [UO_2(Salbz)] > [UO_2(5\text{-MeOSalbz})]$$

Biological activitiy of some of these complexes were studied, and it showed that $[UO_2(5\text{-ClSalbz})(MeOH)]$ 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.

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LIST OF ABBREVIATION

Definition	Abbreviation
δ	chemical shift
A	ampere
ε	extinction coefficient ($M^{-1}cm^{-1}$)
λ	wavelength
°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-boromosalicylidene)-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 Hrtz
Me	methyl
MeOH	methanol
salen	N,N'-bis(salicylaldehyde) ethylenediamine
min	minute
ml	mililitre (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	tetrabutylammuniumperchlorate
IL	intraligand
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. R^1, R^2, and/or R^3 = 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]