

Faculty of Sciences

M.Sc. Thesis In Inorganic Chemistry

SYNTHESIS AND CHARACTERIZATION OF A NANO URANYL SCHIFF BASE COMPLEX AND SYNTHESIS, CHARACTERIZATION AND KINETIC STUDIES OF SOME URANYL SCHIFF BASE COMPLEXES

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September 2012

In The Name of God

IN THE NAME OF GOD

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FAHIMEH DEHGHANI FIRUZABADI

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SHIRAZ

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SEPTEMBER 2012

DEDICATED TO:

MY PARENTS MY SISTERS

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF A NANO URANYL SCHIFF BASE COMPLEX AND SYNTHESIS, CHARACTERIZATION AND KINETIC STUDIES OF SOME URANYL SCHIFF BASE COMPLEXES

$\mathbf{B}\mathbf{Y}$

FAHIMEH DEHGHANI FIRUZABADI

In this work, Schiff base ligands were prepared by condensation of 2-hydroxy1naphtaldehyde with 1,2-ethylenediamine, 1,3-propylenediamine, 1,2-propylenediamine, 1,2-phenylenediamine, 1,4-butylenediamine, 4-methyl-1,2-phenylendiamine, 4-chloro-1,2-phenylendiamine, 4-nitro-1,2-phenylenediamine, 4-carboxyl-1,2-phenylenediamine and their UO₂L complexes were synthesized by the reaction of uranyl acetate with Schiff base ligands. These ligands and complexes were characterized by ¹H NMR, IR spectroscopy, UV-vis. spectrophotometry, X-ray crystallography, TG (thermal gravimetry), CV (cyclic voltammetry), and elemental analysis (C.H.N). For the first time, а nano structure of [UO₂(napht-1,2pr)(MeOH)] was synthesized. Scanning electronmicroscopy (SEM) and transmission electron microscopy (TEM) image showed nano-particles with sizes 16-30 nano-meters. In anti-cancer studies of the uranyl Schiff base complexes, Cell culture and MTT assay were used. Kinetic data of eight uranyl Schiff base complexes were determined spectrophotometrically. In all cases (runs from 10-40±0.1°C), the procedure involves adding a sample of PBu₃ to solutions containing the uranyl complexs. The kinetics was followed at a predetermined wavelength, where the difference in absorption between the substrate and the product was the largest. The pseudo-first-order constants were calculated by fitting data to $\ln[(A_t-A_{\infty})/(A_0-A_{\infty})] =$ $k_{obs}t$ (where A_t =Absorbance at time t; A_0 =Absorbance at t=0; A_{∞} =Absorbance at t= ∞). The second order rate constants k_2 were obtained from the slope of the linear plots of k_{obs}

vs. [PBu₃]. ΔH^{\neq} and ΔS^{\neq} were obtained from the Eyring plots of ln(k₂/T) *vs.* 1/T at four different temperatures.

The second order k₂ rate constants show the following trend:

- 1) $[UO_2(5-Brsalbzph)(CH_3CN)] > [UO_2(salbzph)(CH_3CN)] > [UO_2(5-MeOsalbzph)(CH_3CN)]$
- 2) $[UO_2(4-MeOsalbzph)(CH_3CN)] > [UO_2(5-MeOsalbzph)(CH_3CN)] > [UO_2(3-MeOsalbzph) (CH_3CN)]$
- 3) $[UO_2(5-Brsalbzph)(CH_3CN)] \approx [UO_2(5-Clsalbzph)(CH_3CN)]$
- 4) $[UO_2(napht-1,3pr)(CH_3CN)] > [UO_2(napht-1,2pr)(CH_3CN)]$

The low $\Delta H^{\#}$ values and the large negative $\Delta S^{\#}$ values are compatible with (A) mechanism.

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