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

By

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September 2012

In The Name of God

IN THE NAME OF GOD

Declaration

I Fahimeh Dehghani Firuzabadi (890480), the student of inorganic chemistry, faculty of sciences, declare that this thesis is my own research; everywhere I have used the references, I have referred the complete and accurate address of the reference. In addition, I state that the research and its subject are not repeated and I do not have any privileges to publish its results without Shiraz University license or give them to the others. According to the rules of mental and spiritual, all rights are preserved for Shiraz University.

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MY PARENTS

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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

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In this work, Schiff base ligands were prepared by condensation of 2-hydroxy1-naphtaldehyde 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 UO_2L 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, a nano structure of $[UO_2(napht\text{-}1,2pr)(MeOH)]$ 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±0.1ºC), the procedure involves adding a sample of PBu_3 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. [PBu_3]. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained from the Eyring plots of $\ln(k_2/T)$ *vs*. 1/T at four different temperatures.

The second order k_2 rate constants show the following trend:

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

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

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