



Competition between five different chelates to capture of uranyl ion: Synthesis, spectroscopic, thermal, surface and biological investigations

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ABSTRACT

The uranium ion in various chemical forms is one of the most valuable metals that exists in seawater. To recognize the uranyl ion (UO_2^{2+}) is a longstanding goal for the purposes of environmental remediation, metallurgical extraction, and water purification from seawater. Uranium complexes of the composition $\text{UO}_2\text{L}(\text{NO}_3)_2$, where L is 2-[(5-*o*-chlorophenylazo-2-hydroxybenzylidene)amino]-phenol Schiff base (SB), *N*-(1-naphthyl)ethylenediamine (ND), *N,N,N',N'*-tetramethylethylenediamine (TD), α,α' -bipyridyl (BP), or hexamethylenediamine (HD) were synthesized and characterized by several physicochemical techniques. This study investigated the microstructure properties of these complexes using XRD and SEM techniques. Furthermore, the antimicrobial activity of the complexes was assessed against two types of bacterium and fungus species. The complexes decompose endothermically in a single-to-fourth steps to give a solid powder of UO_2 or UC_x (where $x = 1$ or 2) as the residual product through indefinite intermediates. All of the uranyl complexes seem to possess a hexagonal bipyramidal geometry surrounding the uranium atom.

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1. Introduction

Uranium metal is only the strategic resource for the nuclear industry. It is a radioactive material and must be used in a licensed facility by trained personnel. Uranium is a global contaminant with high toxicity, and the concentration of uranium in seawater is always 3.3 mg/m^3 [1], and extracting uranium from seawater is a challenging problem. Many methods have been developed and tested for the separation, extraction, or remediation of uranium from seawater, phosphate ores and the nuclear fuel cycle process [2–5]. Phosphate ore is important natural sources of fertilizers, and is used widely in chemical industry. In addition, phosphate ore commonly contain relatively high concentrations of useful elements such as uranium, fluorine, and vanadium. Sedimentary phosphate ores tends to have high concentrations of uranium in the range of 50–200 ppm [6–8]. The search for and development of ligands that can effectively and selectively bind uranyl ion (UO_2^{2+}) has great importance in the fields of uranium recovery from seawater, phosphate ores, the nuclear fuel cycle process, chelation therapy for metal poisoning, and uranium mining and purification [9,10]. For this purpose, many ligands, such as phosphonate, sulfocatecholamide, hydroxypyridinone, and the amidoxime functional group, were synthesized and developed

[11–13]. The UO_2^{2+} is important for the environmental chemistry of radioactive elements due to its role as a benchmark system for larger actinides [14]. Furthermore, the UO_2^{2+} is important for its relative abundance in nature and impacts on the biosphere. Recently, UO_2^{2+} was used in the fabrication of uranyl organic framework materials that were used as absorbent materials for actinides and their fission products were generated in the nuclear fuel cycle [15,16]. The chemical interaction behaviors of the UO_2^{2+} are similar to those of d-block divalent cations, both of which form complexes with a variety of neutral molecules and anions [17–19]. The $(\text{O}=\text{U}=\text{O})^{2+}$ group in uranyl complexes is linear, and the coordination occurs on or near the equatorial plane, forming a hexagonal, pentagonal bi-pyramidal, or square bi-pyramidal geometry [20,21]. Additionally, metal chelates of nitrogen-containing ligands or Schiff bases have a wide range of applications [22–26].

In this study, I select four nitrogen-containing ligands that have simple structures: *N*-(1-naphthyl)ethylenediamine (ND), *N,N,N',N'*-tetramethylethylenediamine (TD), α,α' -bipyridyl (BP), and hexamethylene diamine (HD). I also synthesized a new Schiff base with the chemical name 2-[(5-*o*-chlorophenylazo-2-hydroxybenzylidene)amino]-phenol (SB) in order to observe the ability of the five ligands to react with the UO_2^{2+} . I aimed, through the selection of these five ligands, to cover the different types of donating nitrogen atoms, like the azomethine group for the synthesized Schiff base ligand (SB), primary amine-like HD ligand, secondary amine-like ND ligand, tertiary amine-

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like TD ligand, and aromatic amine-like BP ligand. This study focused on the following objectives:

- Synthesizing a novel 2-[(5-*o*-chlorophenylazo-2-hydroxybenzylidene)amino]-phenol Schiff base (SB).
- Synthesizing a series of uranyl complexes (UO_2^{2+}) with different nitrogen chelates, including ND, TD, BP, and HD, as well as with the synthesized Schiff base (SB).
- Characterizing the synthesized uranyl complexes by their elemental and spectroscopic data and their molar conductance measurements.
- Obtaining the thermal properties of the synthesized complexes using TG/DTG analysis.
- Observing the microstructure of the synthesized complexes using different physical methods, such as X-ray diffraction (XRD) and scanning electron microscopy (SEM).
- Examining the antimicrobial activity of synthesized complexes against two Gram-positive bacteria and two Gram-negative bacteria as well as two fungi.

2. Experimental

2.1. Chemicals

Uranyl (VI) nitrate hexahydrate (purity; 98%), *o*-chloroaniline (purity; $\geq 98\%$), *o*-aminophenol (purity; 99%), salicylaldehyde (purity; 98%), *N*-(1-naphthyl)ethylenediamine (ND) (purity; $\geq 98\%$), *N,N,N',N'*-tetramethylethylenediamine (TD) (purity; $\geq 99.5\%$), α,α' -bipyridyl (BP) (purity; $\geq 99\%$), and hexamethylenediamine (HD) (purity; 98%) were obtained from Sigma–Aldrich Chemical Company (USA) and were used as received. Solvents were obtained from Merck (Darmstadt, Germany) or BDH (UK) and used without special treatment.

2.2. Synthesis of the SB Schiff base ligand

The 2-[(5-*o*-chlorophenylazo-2-hydroxybenzylidene)amino]-phenol Schiff base (SB) (Fig. 1) was obtained by a two-step procedure as follows:

i. Synthesis of 5-arylazo-salicylaldehyde compound

5-Arylazo-salicylaldehyde compound was prepared by dissolving *o*-chloroaniline (50 mmol) in 6.0 mL of 37% hydrochloric acid and distilled water (30 mL). The solution was then cooled to 0–5 °C in an ice bath and maintained at this temperature. Sodium nitrite (40 mmol, 2.8 g) solution in distilled water (30 mL) was then added in drops. The mixture was stirred for 30 min to produce the diazonium salt. The solution of the diazonium salt was coupled with salicylaldehyde in alkaline media at the *para* position to the hydroxyl group at pH values of 7–9 and temperatures of 0–5 °C [27]. The mixture was recrystallized several times; the pH value was decreased to ~ 3 and then left overnight. The diazo product was filtrated, washed with a small portion of diethyl ether to extract all organic impurities, and

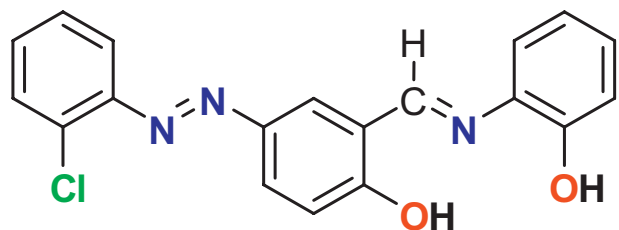


Fig. 1. Structure of 2-[(5-*o*-chlorophenylazo-2-hydroxybenzylidene)amino]-phenol Schiff base (SB) ligand.

then dried under vacuum at 70 °C. The purity of the diazo product was evaluated by thin layer chromatography.

ii. Synthesis of the Schiff base

50-mL methanol solution of *o*-aminophenol (50 mmol) was mixed with a solution of 5-arylazo-salicylaldehyde (50 mmol) in water (100 mL) under reflux for 2 h at 70 °C on a hot plate [28]. After cooling, the precipitate was filtered, washed several times with methanol and diethyl ether to remove all organic impurities, and dried in vacuo over calcium chloride. The purity of the ligand was evaluated using thin layer chromatography, and the composition was confirmed by elemental analysis CHN and (IR, mass, and 1H NMR) spectra [29].

2.3. Synthesis of the uranyl (UO_2^{2+}) complexes

A solution of uranyl (VI) nitrate salt (1 mmol in 25 mL methanol solvent) was added gradually to a stirred methanol solution of the nitrogen ligands: SB (Fig. 1), ND TD, BP and HD (Fig. 2) (1 mmol in 25 mL methanol solvent). The reaction mixtures were refluxed at 60 °C with further stirred for 1 h to ensure the completion and precipitation of the formed complexes. The precipitated yellow solid complexes were filtered and washed several times with diethyl ether, and they were dried under vacuum over anhydrous $CaCl_2$.

2.4. Physical and spectroscopic measurements

The micro-analytical analyses of %C, %H, and %N percentages were calculated using a Perkin Elmer CHN 2400 (USA). The uranium contents were determined gravimetrically by converting the synthetic complexes to its UO_2 black powder stable oxide form. The molar conductivities of all uranyl complexes with concentrations of 10^{-3} mol/cm³ in DMSO solvent were measured using a Jenway 4010 conductivity meter. The IR spectra with KBr discs were measured using a Bruker FT-IR Spectrophotometer (4000–400 cm^{-1}), while the Raman laser spectra were measured on the Bruker FT-Raman with a 50-mW (4000–50 cm^{-1}) laser. The electronic absorption spectra were recorded in DMSO solvent within 200–800 nm using a UV2–Unicam UV/vis Spectrophotometer with a 1.0-cm quartz cell. The 1H NMR spectra were recorded as DMSO solutions using a Bruker 600 MHz spectrometer with TMS as the internal standard. The thermal studies were carried out using a Shimadzu thermogravimetric analyzer at a heating rate of 10 °C min^{-1} under an air atmosphere to 800 °C. The SEM images were obtained using a Jeol Jem-1200 EX II electron microscope at an acceleration voltage of 25 kV. Energy dispersive X-ray detection (EDX) was

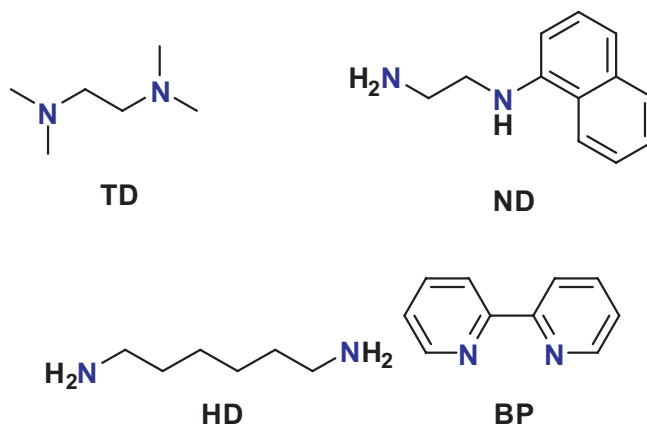


Fig. 2. Structures of *N*-(1-naphthyl)ethylenediamine (ND), *N,N,N',N'*-tetramethylethylenediamine (TD), α,α' -bipyridyl (BP) and hexamethylenediamine (HD) ligands.

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