Available online at www.sciencedirect.com
ScienceDirect
Polyhedron 27 (2008) 1408–1414
POLYHEDRON
www.elsevier.com/locate/poly

Synthesis, molecular and supramolecular structure, spectroscopy and electrochemistry of a dialkoxo-bridged diuranyl(VI) compound

Susanta Hazra [a], Samit Majumder [a], Michel Fleck [b], Sasankasekhar Mohanta [a,*]

[a] *Department of Chemistry, University of Calcutta, 92 A. P. C. Ray Road, Kolkata 700 009, India*
[b] *Institute for Mineralogy and Crystallography, University of Vienna, Althanstr. 14, A-1090 Vienna, Austria*

Received 20 November 2007; accepted 10 January 2008
Available online 7 March 2008

Abstract

The synthesis, molecular and supramolecular structure, spectroscopy and electrochemistry of a dialkoxo-bridged diuranyl(VI) compound $[(UO_2)_2(L)_2(\text{dimethylformamide})_2]$ (**1**) derived from the Schiff base ligand H_2L, obtained on condensation of 3-methoxysalicylaldehyde with 2-aminoethanol, have been described. The compound has been characterized by IR, UV–Vis, NMR and mass spectra, as well as by single crystal X-ray structure determination. The title compound crystallizes in the monoclinic $P2_1/n$ space group with the following unit cell parameters $a = 10.5713(2)$ Å, $b = 11.9895(2)$ Å, $c = 12.9372(2)$ Å, $\beta = 102.773(3)°$ and $Z = 2$. The structure of **1** reveals that it is a dialkoxo-bridged dinuclear compound of uranium(VI) containing two deprotonated ligands, $[L]^{2-}$, two dimethylformamide (dmf) molecules and two UO_2^{2+} centers. The coordination geometry around the uranium(VI) center is distorted pentagonal bipyramidal; two uranyl oxygens occupy the axial positions, while the basal pentagonal plane is defined by a phenoxo oxygen, two bridging alkoxo oxygens, one imine nitrogen, and one dmf oxygen. Three C–H···O type hydrogen bonds involving one uranyl oxygen, two dmf hydrogens and the imine hydrogen link the dinuclear units into a two-dimensional network. The ESI-MS spectrum of **1** in dimethylsulfoxide exhibits two peaks at $m/z = 464.17$ and 927.26, which are assignable to $[(UO_2)_2L_2H]^+$ (60%) and $[(UO_2)_2LH]^+$ (100%) cations, respectively. Cyclic voltammetric measurements of **1** reveal that the uranium(VI) center is reduced quasireversibly at $E_{1/2} = -1112$ mV with $\Delta E_P = 97$ mV.

Keywords: Uranyl; Diuranyl; Cyclic voltammetry; Hydrogen bond; Two-dimensional; Mass spectrum

1. Introduction

Actinide chemistry is important due to some practical concerns like the extraction of actinides from sea water, removal of actinides from soil, ground water, human beings, and radioactive waste [1–7]. However, although the chemistry of the 5f elements has been highly considered in recent years and is under development [1–30], the number of coordination compounds of actinides is much less than that of transition metals and lanthanides. Again, amongst the actinides the chemistry of uranium has been more explored [1–30]. It should be mentioned that a number of complexes of uranium in different oxidation states (III, IV, V and VI) have been reported in recent years [1–30].

Due to the variable oxidation states of the uranium center (III, IV, V and VI), electrochemical studies [8–12] of uranium complexes are valuable to understand the influence of the ligand environment on the relative stability of the U^{III}, U^{IV}, U^{V} and U^{VI} species in solution.

The species of uranium in the VI oxidation state is the linear uranyl dication, UO_2^{2+}. It is known that the oxygen atoms of UO_2^{2+} are able to engage in hydrogen bonding interactions [13]. Evidently, in addition to the above mentioned practical concerns, compounds of the uranyl dication may also be an appealing member to develop supramolecular architectures [31–38]. However, this possibility has not been well explored in previously reported uranyl complexes.

---

[*] Corresponding author. Tel.: +91 33 23508386; fax: +91 33 23519755.
E-mail address: sm_cu_chem@yahoo.co.in (S. Mohanta).

0277-5387/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2008.01.029

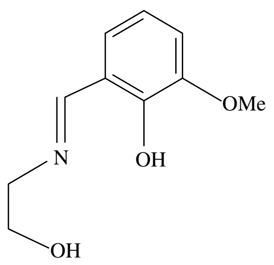

Chart 1. Chemical structure of H_2L.

A few Schiff base ligands have been previously utilized to derive uranium compounds. Salmon et al. have reported a number of mono-, tri-, tetra- and hexanuclear uranium(IV) complexes derived from compartmental Schiff base ligands obtained by the condensation of salicylaldehyde or substituted salicylaldehydes with diamines [14–16]. A mononuclear uranyl(VI) compound in a similar ligand environment has been reported by Ikeda et al. [8]. Using a tridentate ligand obtained by the condensation of 3-methoxysalicylaldehyde and *o*-aminophenol, a diphenoxo-bridged diuranyl(VI) compound has been reported by Reedijk and coworkers [17]. A series of dialkoxo-bridged diuranyl(VI) compounds derived from tridentate ligands obtained by the condensation of salicylaldehyde or substituted salicylaldehydes and substituted 2-aminoethanol have been reported by Rao and coworkers [18]. Herein, we report the synthesis, molecular and supramolecular structure, spectroscopy and electrochemistry of a dialkoxo-bridged diuranyl(VI) compound $[(UO_2)_2(L)_2(\text{dimethylformamide})_2]$ (**1**) derived from the Schiff base ligand (H_2L; Chart 1) obtained by the condensation of 3-methoxysalicylaldehyde with 2-aminoethanol.

2. Experimental

2.1. Materials and physical methods

All the reagents and solvents were purchased from commercial sources and were used as received. The Schiff base ligand H_2L was prepared by condensing 3-methoxysalicylaldehyde with 2-aminoethanol in methanol. The syntheses of the ligand and title compound were performed in open atmosphere. Elemental (C, H and N) analyses were performed on a Perkin–Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm^{-1} on a Perkin–Elmer RXIFT spectrophotometer with the samples as KBr disks. Electronic spectra were obtained with a Hitachi U-3501 spectrophotometer. The electrospray ionization mass spectra were recorded on a Micromass Qtof YA 263 mass spectrometer. The ^1H NMR (300 MHz) spectra were recorded on a Bruker Avance DPX-300 spectrometer. Cyclic voltammetric (CV) measurement was done using a Bioanalytical System BAS 100B electrochemical analyzer. The concentration of the supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was 0.1 M, while that of the complex was 1 mM. Cyclic voltammetric measurement in dimethylsulfoxide solution was carried out with a three-electrode assembly comprising a glassy carbon disk working electrode, a platinum auxiliary electrode and an aqueous Ag/AgCl reference electrode. The reference electrode was separated from the bulk solution using a TBAP salt bridge in acetonitrile. Under the experimental conditions, the $E_{1/2}$ value of the ferrocene/ferrocenium couple was 400 mV.

Table 1
Crystallographic data for **1**

Formula	$C_{26}H_{36}N_4O_{12}U_2$
Molecular weight	1072.65
Crystal color	red
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.5713(2)
b (Å)	11.9895(2)
c (Å)	12.9372(2)
β (°)	102.773(3)
V (Å^3)	1599.14(5)
Z	2
Temperature (K)	293(2)
2θ	8.152–69.944
μ (mm^{-1})	10.179
$D_{calc.}$ ($g\ cm^{-3}$)	2.228
$F(000)$	1000
Scan mode	φ- and ω-scans
Number of frames	510
Scan time per frame (s)	30
Rotation width (°)	2
Crystal-detector-dist. (mm)	28
Absorption-correction	multi-scan
T_{min}	0.7499
T_{max}	0.9051
Index ranges	$-17 \leqslant h \leqslant 17$, $-19 \leqslant k \leqslant 18$, $-20 \leqslant l \leqslant 20$
Reflections collected	12911
Independent reflections ($F_o > 4\sigma(F_o)$)	7002
R_1^a/wR_2^b ($F_o > 4\sigma(F_o)$)	0.0287/0.0706
R_1^a/wR_2^b (for all F_o^2)	0.0412/0.0754

[a] $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

2.2. Synthesis of $[(UO_2)_2(L)_2(dmf)_2]$ (1)

To a stirred dimethylformamide (dmf) solution (40 ml) containing H_2L (0.098 g, 0.5 mmol) and uranyl nitrate hexahydrate (0.251 g, 0.5 mmol) was added a dmf solution (10 mL) of triethylamine (0.101 g, 1 mmol). The resulting red solution was filtered to remove any suspended particles and the filtrate was kept at room temperature. After a few hours a red crystalline compound containing diffractable single crystals were deposited, then collected by filtration and washed with methanol. Yield: 0.24 g (90%). *Anal.* Calc. for $C_{26}H_{36}N_4O_{12}U_2$: C, 29.11; H, 3.38; N, 5.22. Found: C, 29.20; H, 3.46; N, 5.31%. IR (KBr/cm^{-1}): υ(C=N), 1636 vs; υ(O=U=O), 891 m.