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Novel Dinuclear Uranyl Complexes with Asymmetric Schiff Base Ligands: Synthesis, Structural Characterization, Reactivity, and Extraction Studies

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The reaction of uranyl nitrate with asymmetric [3O, N] Schiff base ligands in the presence of base yields dinuclear uranyl complexes, $[UO_2(HL1)]_2{\cdot}DMF$ (**1**), $[UO_2(HL2)]_2{\cdot}2DMF{\cdot}H_2O$ (**2**), and $[UO_2(HL3)]_2{\cdot}2DMF$ (**3**) with 3-(2-hydroxybenzylideneamino)propane-1,2-diol (H_3L1), 4-((2,3-dihydroxypropylimino)methyl)benzene-1,3-diol (H_3L2), and 3-(3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)propane-1,2-diol (H_3L3), respectively. All complexes exhibit a symmetric U_2O_2 core featuring a distorted pentagonal bipyramidal geometry around each uranyl center. The hydroxyl groups on the ligands are attached to the uranyl ion in chelating, bridging, and coordinate covalent bonds. Distortion in the backbone is more pronounced in **1**, where the phenyl groups are on the same side of the planar U_2O_2 core. The phenyl groups are present on the opposite side of U_2O_2 core in **2** and **3** due to electronic and steric effects. A similar hydrogen-bonding pattern is observed in the solid-state structures of **1** and **3** with terminal hydroxyl groups and DMF molecules, resulting in discrete molecules. Free aryl hydroxyl groups and water molecules in **2** give rise to a two-dimensional network with water molecules in the channels of an extended corrugated sheet structure. Compound **1** in the presence of excess $Ag(NO_3)$ yields $\{[(UO_2)(NO_3)(C_6H_4OCOO)](NH(CH_2CH_3)_3)\}_2$ (**4**), where the geometry around the uranyl center is hexagonal bipyrimidal. Two-phase extraction studies of uranium from aqueous media employing H_3L3 indicate 99% reduction of uranyl ion at higher pH.

Introduction

Interest in the coordination chemistry of uranium has recently increased for several reasons.[1−4] The primary reasons are the reduction of nuclear waste generated as spent reactor fuel[5] along with the extraction of uranium from seawater, groundwater, soil, and waste remediation from actinide decorporation.[6−8] Uranium and other actinides are major contributors to the long-term radioactivity of nuclear wastes. The separation of actinides from the lanthinides is most difficult due to their similar oxidation state and ionic radii.[9] Various ligand systems have been used for the selective extraction of uranium including organic phosphorus oxides,[10] crown ethers, azacrowns, calixarenes,[11,12] and Schiff base ligands.[13] Macrocyclic ligands often form discrete, solvated uranyl salts without being incorporated in the cyclic compartment or else form polymeric arrays with weak interactions.[12,14,15] Calixarenes and modified calixarenes have been investigated for use as extractants, yet these ligands are often

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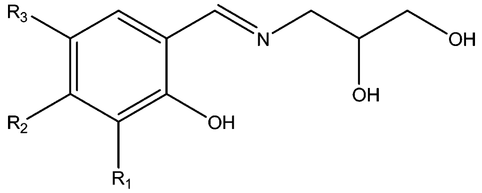
either too rigid or too flexible for optimal complexations.[6,16−20] This leads to the potential use of Schiff base ligands for the selective coordination of uranyl ions. These ligands possess a multidentate mixed aza- and oxo-core and a flexible backbone. The use of Schiff base ligands for uranyl complexation has been previously reported.[13,21] Extraction studies employing multidentate Schiff base ligands have shown improved efficiency of quadridentate ligand in acidic pH range (1.5−4.5) over bidentate Schiff bases.[22] Synergy was observed in extractions using a mixture of H_2Salen (*N*,*N*′-ethylenebis(salicylidenimine)) and neutral donor ligands such as tri-*n*-octylphosphine oxide (TOPO), triphenyl phosphine oxide (TPPO), and triphenyl arsine oxide.[22]

The general coordination motif of uranyl Schiff base complexes involve the ligand bound in a tetradentate fashion along the equatorial axis of the uranyl ion and a solvent molecule occupying the fifth coordinate site in the equatorial position.[23,24] The presence of the solvent at the fifth coordination site can play an important role in the activation of the substrate in catalysis for acyl transfer,[25] Michael-type addition of thiols,[26] and molecular recognition of urea derivatives, pyridine derivatives, amines, quinolines, nitriles, and other anions.[27,28] The presence of a ligating agent (H_2O, MeOH, EtOH, DMF, DMSO, Py, NO_3^-) tends to form solvated discrete molecules, and this limits the ability of Schiff base to be used as an extraction agent in aqueous media. Hence, for selective uranyl extraction, it is important that the complex be neutral and its coordination be complete without ligating agents.[29]

We have synthesized and characterized novel asymmetric [3O, N] Schiff base ligands (Figure 1) and their uranyl complexes. To our surprise, mononuclear species [UO_2(ligand)(solvent)] were not observed in these cases. In a recent study, it has been shown that uranyl Schiff base complexes, [UO_2(Schiff base)(DMF/Py/MeOH/EtOH)] exist as dimers ([UO_2(Schiff base)]$_2$) in nonpolar solvents with phenolic oxygen involved in the bridging.[24] It can be assumed that the labile backbone of the ligand force the formation of dinuclear species. Most of the dinuclear uranyl complexes reported in the literature involve an extra ligating solvent molecule, for example, H_2O, NO_3^-, SO_4^{2-}, Py, THF.[30−35]



Ligands	R_1	R_2	R_3
H_3L1	H	H	H
H_3L2	H	OH	H
H_3L3	t-Butyl	H	t-Butyl

Figure 1. Structures of H_3L1, H_3L2, and H_3L3.

Two-phase solution extraction studies with M/L in 1:2 ratios has been performed in chloroform and hexane under various pH conditions (1−5). Similar study with aminoalcoholbis(phenolate) [3O, N]-based ligands have been performed, where mono- and dinuclear uranyl complexes have been reported with 85−93% transfer of uranyl ion from the aqueous to the organic phase.[31] The advantage of the ligands reported here is the absence of a ligating molecule coordinated to the metal center, making them good candidates for selective extraction of actinides from aqueous sources.

Experimental Section

General Procedure. $UO_2(NO_3)_2{\cdot}6H_2O$, 3-amino-1,2-propanediol alcohol, salicylaldehyde, 2,4-dihydroxybenzaldehyde, and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde were purchased from Acros and used as received. The ^{1}H and ^{13}C NMR were recorded on a Bruker AV 400 spectrometer operated at 400 MHz with DMSO-d_6 and MeOH-d_4 as solvents with tetramethylsilane as the reference. All melting points were recorded on a Mel-temp II melting point apparatus, and the values are uncorrected. The IR data were recorded as KBr pellets on a SHIMSDZU, Inc. IR, Prestige-21 Fourier transform infrared spectrophotometer in the range 400−4000 cm^{-1}. Electrospray ionization mass spectrometry was performed on a Micromass QTOF mass spectrometer (Waters Corp, Milford, MA). All UV data was collected using a Cary 50 UV−vis spectrophotometer with a xenon lamp in the range 200−1200 nm.

X-ray Crystallography. Crystals of compounds **1**−**3** were obtained in good yield from DMF by slow evaporation at room temperature. X-ray diffraction data for **1**−**4** were collected at −80 °C on a Bruker SMART APEX CCD X-ray diffractometer unit using Mo Kα radiation from crystals mounted in Paratone-N oil on glass fibers. SMART (v 5.624) was used for preliminary determination of cell constants and data collection control. Deter-

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Table 1. Crystal Data for Compounds **1**−**4**

compounds	**1**	**2**	**3**	**4**
empirical formula	$C_{10.4}H_{14.4}N_{1.6}O_{4.8}U_{.8}$	$C_{13}H_{18}N_2O_{7.5}U$	$C_{24}H_{41}N_3O_7U$	$C_{13}H_{20}N_2O_8U$
fw	212.22	560.32	721.63	570.34
λ (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P21$	$P21/c$	$P21/c$
a (Å)	33.9430(2)	7.1167(6)	10.2356(9)	8.4730(1)
b (Å)	8.2601(5)	13.1937(1)	15.8225(1)	13.770(2)
c (Å)	11.3377(7)	17.8071(1)	35.4890(3)	15.428(2)
β (deg)	94.62(1)	97.43(2)	94.00(2)	104.777(4)
V (Å^3)	3168.4(3)	1658.0(2)	5733.6(8)	1740.4(5)
Z	10	4	8	4
ρ_{calcd} (mg/m^3)	2.249	2.245	1.672	2.177
abs coeff (mm^{-1})	10.275	9.830	5.705	9.368
F(000)	2000	1048	2832	1072
cryst size (mm^3)	0.04 × 0.04 × 0.02	0.1 × 0.07 × 0.03	0.07 × 0.05 × 0.02	0.1 × 0.05 × 0.03
reflns collected	15 604	13 763	57 211	11 653
indep reflns	3917 (R_{int} = 0.0403)	7763 (R_{int} = 0.0466)	14 193 (R_{int} = 0.0435)	2513 (R_{int} = 0.1515)
refinement method	full-matrix least squares on F^2			
GOF of F^2	1.052	0.907	1.025	0.900
final R indices [$I > 2\sigma(I)$]	R1 = 0.0294 wR2 = 0.0685	R1 = 0.0411 wR2 = 0.0743	R1 = 0.0461 wR2 = 0.1168	R1 = 0.0670 wR2 = 0.1440
R indices (all data)	R1 = 0.0369 wR2 = 0.0709	R1 = 0.0456 wR2 = 0.0773	R1 = 0.0709 wR2 = 0.1264	R1 = 0.1113 wR2 = 0.1571
largest diff peak and hole (e/Å^3)	1.914 and −0.866	1.777 and −1.112	3.036 and −1.712	4.467 and −0.925

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1**−**3**[a]

		1	
U1−O2	1.783(3)	U1−O1	1.785(3)
U1−O3	2.222(4)	U1−O4#1	2.330(3)
U1−O4	2.377(3)	U1−O5	2.472(3)
U1−N1	2.556(4)	U1−U1#1	3.8794(4)
O2−U1−O1	179.75(1)	O2−U1−O3	91.97(1)
		2	
U1−O2	1.767(8)	U1−O1	1.776(8)
U2−O7	1.768(8)	U2−O8	1.777(8)
U1−O3	2.261(6)	U1−O4	2.299(6)
U1−O10	2.354(7)	U1−O11	2.474(8)
U1−N1	2.508(9)	U2−N2	2.547(9)
U1−U2	3.8633(5)		
O2−U1−O1	177.3(3)	O7−U2−O8	178.9(4)
		3	
U1−O1	1.767(5)	U1−O2	1.777(5)
U2−O6	1.755(4)	U2−O7	1.774(4)
U1−O3	2.237(4)	U1−O4#2	2.327(4)
U1−O4	2.384(4)	U1−O5	2.483(4)
U1−N1	2.527(5)	U2−N2	2.533(5)
U1−U1#2	3.9182(5)	U2−U2#3	3.9321(5)
O1−U1−O2	178.2(2)	O6−U2−O7	178.7(2))

[a] #1 = −x, y, −z + 1/2; #2 = −x, −y + 2, −z; #3 = −x, −y + 1, −z.

mination of integrated intensities and global cell refinement were performed with the Bruker SAINT software package using a narrow-frame integration algorithm. The program suite SHELXTL (v 5.1) was used for space group determination, structure solution, and refinement.[36] Refinement was performed against F^2 by weighted full-matrix least-square, and empirical absorption correction (SADABS[37]) were applied. H atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Crystal data, selected bond distances, and angles are provided in Tables 1 and 2.

Uranyl Extraction. Two-phase extraction studies ($CHCl_3/H_2O$ and hexane/H_2O) were performed to determine the extraction capability for the removal of UO_2^{2+} ion from aqueous solution. The ligand H_3L3 (8 × 10^{-3} M) which is quantitatively soluble in chloroform and hexane was solely used for extraction studies. Fresh solutions of $UO_2(NO_3)_2{\cdot}6H_2O$ (4 × 10^{-3} M) were prepared in deionized (DI) water, and the pH was adjusted with HNO_3 and KOH. The experimental setup was as follows. UO_2^{2+} solution (5 mL) was added to the organic phase containing 5 mL of H_3L3 in scintillation vials and shaken for 20 s. The absorption spectra of the aqueous phase were determined at 1−7, 24, and 24 h stirring (only $CHCl_3$). Furthermore, separate vials containing organic solvent without ligand and UO_2^{2+} at respective pH were prepared for blanks. Stability of the ligand H_3L3 in the organic phase was studied by placing equal amount of water layer of pH 1−5. The calculations for the reduction of uranyl ion from the aqueous media were done based on λ_{max} for UO_2^{2+} (415 nm).[38] Presence of an additional peak due to the formation of uranyl Schiff base complex in aqueous media was not detected.

Schiff Base and Uranium Complexes. The ligands were synthesized by heating amine and the respective aldehyde in absolute ethanol at reflux temperature. Complexes **1**−**3** were synthesized by refluxing ethanolic solution containing ligands (1 mmol), triethylamine (1 mmol), and $UO_2(NO_3)_2{\cdot}6H_2O$ (1 mmol) for 5−6 h. The resulting precipitates were filtered, washed with a cold MeOH/$CHCl_3$ (1:1) mixture, and dried under vacuum. The precipitates were dissolved in minimum amount of hot DMF and left at room temperature, yielding crystals. Addition of $Ag(NO_3)$ (2 mmol) to **1** (0.5 mmol) in DMF containing triethylamine (1 mmol) yielded a silver-brown precipitate, which was not soluble in common solvents. The precipitate was washed with ethanol, which yielded a few crystals of **4** ($\{[(UO_2)(C_6H_4OCOO)(NO_3)](NH(CH_2CH_3)_3)\}_2$).

Synthesis of 3-(2-Hydroxybenzylideneamino)propane-1,2-diol (H_3L1). Yield = 80%, mp = 86−88 °C, ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 3.40 and 3.75 (m, $CH_2{-}CH{-}CH_2$, 5H); 6.86 and 7.42 (m, C_6H_4, 4H), 8.48 (s, CHO, 1H).

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Synthesis of 4-((2,3-Dihydroxypropylimino)methyl)benzene-1,3-diol (H_3L2). Yield = 90%, mp = 135 − 137 °C, ^1H NMR (400 MHz, DMSO-d_6, ppm): 3.47 and 3.71 (m, $CH_2-CH-CH_2$, 5H), 6.27 and 7.18 (m, C_6H_3, 3H), 8.27 (s, CHO, 1H).

Synthesis of 3-(3,5-Di-*tert*-butyl-2-hydroxybenzylideneamino)-propane-1,2-diol (H_3L3). Yield = 95%, ^1H NMR (400 MHz, DMSO-d_6, ppm): 1.37 (m, $C(CH_3)_3$, 18H), 3.49 and 3.72 (m, $CH_2-CH-CH_2$, 5H), 7.27 (m, C_6H_2, 2H), 8.47 (s, CHO, 1H).

Synthesis of $[UO_2(HL1)]_2 \cdot DMF$ (1). Yield = 0.7 g (70%), mp > 200 °C, ^1H NMR (400 MHz, DMSO-d_6, ppm): 4.3 and 4.8 (m, $CH_2-CH-CH_2$, 5H), 7.0 and 7.6 (m, C_6H_4, 4H), 9.5 (s, CHN, 1H). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): 42 (CH_2-N), 63 (CH_2-O), 68 (CH−O), 120−135 (phenyl), 169 (C═N). IR (KBr, cm^{-1}): 3450, 2937, 1629, 1547, 1382, 1260, 918, 801. ESI-MS (+ve): 926 $(M)^+$ (30%), 463 $(M/2)^+$ (62%).

Synthesis of $[UO_2(HL2)]_2 \cdot 2DMF.H_2O$ (2). Yield = 0.8 g (72%), mp > 200 °C, ^1H NMR (400 MHz, DMSO-d_6, ppm): 4.3−4.8 (m, $CH_2-CH-CH_2$, 5H), 6.5−7.4 (m, C_6H_3, 3H), 9.3 (s, CHN, 1H), 10.2 (s, 1H, OH). ^{13}C NMR (400 MHz, DMSO-d_6): 42 (CH_2-N), 63 (CH_2-O), 68 (CH−O), 106−164 (phenyl), 171 (C═N). IR (KBr, cm^{-1}): 3455, 2937, 1621, 1559, 1449, 1383, 1224, 901, 801. ESI-MS (+ve): 552 $(M/2)^+$ (10%).

Synthesis of $[UO_2(HL3)]_2 \cdot 2DMF$ (3). Yield = 0.8 g (63%), mp > 250 °C, ^1H NMR (400 MHz, $CDCl_3/CD_3OD$): 1.3 and 1.7 (s, $(-C(CH_3)_3)_2$, 18H), 4.9−5.1 (m, $CH_2-CH-CH_2$, 5H), 7.3 and 7.7 (m, C_6H_2, 2H), 9.4 (s, CHN, 1H). ^{13}C NMR (400 MHz, $CDCl_3/CD_3OD$): 30, 31, and 34, 35 ($(-C(CH_3)_3)_2$, 46 (CH_2-N), 68 (CH_2-O), 72 (CH−O), 120−167 (phenyl), 171 (C═N). IR (KBr, cm^{-1}): 3408, 2953, 1624, 1549, 1384, 1220, 890, 801. ESI-MS (+ve): 646 $(M/2)^+$ (82%).

Results and Discussion

The synthesis of H_3L1 has been reported previously as an intermediate in the purification of 3-amino-1,2-propanediol.[39] The bright orange Schiff base ligands were obtained as solids (H_3L1, H_3L2) or an oil (H_3L3) in quantitative yields. Ligands H_3L1 and H_3L2 were washed with cold methanol and dried to obtain pure compound. Crude H_3L3 was dissolved in $CHCl_3$ and washed with DI water, and the organic solvent was dried with anhydrous $MgSO_4$ and subsequently removed to obtain pure compound. The ligands are bright yellow in color, stable in air, and soluble in a range of solvents. The uranyl complexes have been obtained in quantitative yield (≈70%) by combining the appropriate Schiff base with hexahydrated $UO_2(NO_3)_2$ in absolute ethanol as yellow (**1**, **2**) and reddish-brown precipitate (**3**). The orange-colored crystals suitable for X-ray diffraction studies were obtained by slow evaporation of saturated DMF solution containing respective complexes.

Crystallography data for structural analysis of compounds **1**−**3** and **4** have been deposited with the Cambridge Crystallographic Data Center as CCDC Nos. 642640−642642 and 645794, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (phone + 44 1223 336408; fax + 44 1223 336033).

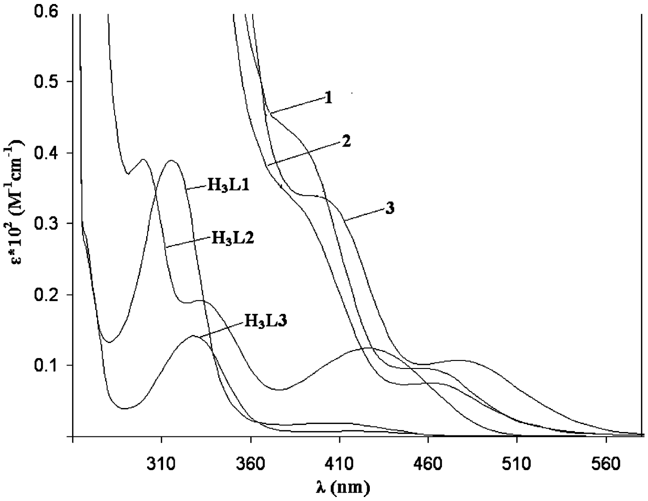

Figure 2. Absorption spectra of ligands and **1**−**3** (5×10^{-2} M) in DMF.

Spectroscopy. In ^1H NMR spectra, a significant shift in the imine CH═N proton is observed between the free ligands (8.2−8.4 ppm) and metal complexes (9.2−9.5 ppm), indicating involvement of the lone pairs on nitrogen with metal center. Similarly, in the IR spectra of **1**−**3** a strong peak around 1620 cm^{-1} (free ligands 1640 cm^{-1}) indicates coordinated imine nitrogen.[30,40] Coordination through the phenolic hydroxyl unit is shown by the shift in the C−O band for uranyl complexes (1220 cm^{-1}) compared to the free ligands (1260 cm^{-1}).[41] The hydroxyl peaks are difficult to assign due to the presence of covalent, bridging, and coordinate covalent bonding. A broad peak around 3400 cm^{-1}, however, is indicative of presence of hydroxyl group. The strong bands at nearly 900 and 800 cm^{-1} due to the asymmetric and symmetric UO_2 stretching are characteristic of linear uranyl ion in the complex.[40,42]

The electronic spectra of the ligands and their complexes in DMF are shown in Figure 2. A red-shift in the spectra of compounds **1**−**3** (λ_{max} at 390, 380, and 400 nm and shoulders at 460 (**1** and **2**) and 480 nm (**3**)) compared to the free ligands (λ_{max} at 300, 314, and 330 nm) signify the formation of the uranyl complex. Similar bands have been reported for multidentate hydroxyl-containing uranyl complexes (390 and 450 nm).[35] The absorption bands for the ligands around 300 nm are due to the $\pi \rightarrow \pi^*$ transition of the imine group.[41] In **1**−**3**, the red-shift in the bands is due to the imine coordination and LMCT (5f ← oxygen 2p).

Crystal Structures. The solid-state structures of compounds **1**−**4** were characterized by means of single X-ray crystallography. There are two molecules of **3** in the asymmetric unit of its crystal structures with noticeable difference in the bond distances despite similar environment around uranyl center (Table 2). The geometry around the uranyl atoms in **1**−**3** is closest to pentagonal-bipyrimidal with axial O═U═O moiety, four oxygen atoms, and a nitrogen atom in equatorial position. The ligand oxygen atoms are

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involved in the coordination with metal center through covalent, bridging, and coordinate covalent bonds. This is in contrast to the uranyl complexes containing multidentate hydroxyl groups, where one or more hydroxyl groups (not coordinated to metal center) are observed. For example, in mononuclear and dinuclear uranyl complexes with aminoalcoholbis(phenolate)-[31] and tris(hydroxyl)methylamine-based[35] ligands, the coordination around the metal center is completed by a ligated solvent molecule. The free hydroxyl groups are involved in intermolecular hydrogen bonding, generating an extended structure. The uranyl oxygen distance in **1** (av 1.78 Å) are slightly longer than the corresponding distances observed in **2** and **3** (av 1.77 Å). The $U-N_{imi}$ distance (2.556(4) Å) in **1** is significantly longer than those observed in **2** and **3** (2.508(9)−2.547(9) Å).

These distances are typical of the corresponding distances reported for other uranyl Schiff base complexes.[24,43,44] The $U-O_{phe}$ distances in **1** (2.222(4) Å) and **3** (2.232(4)/2.237(4) Å) are symmetrical in contrast to unsymmetrical distances observed in **2** (2.189(6) and 2.261(6) Å). The discrepancy in the distances in **2** is due to the hydrogen bonds involving phenolic groups. These distances are also in the range observed for similar compounds (2.231−2.296 Å).[35] The bridging $U-O_{br}$ distances in **1** (2.330(3) and 2.377(3) Å), **2** (av 2.314 and 2.356 Å), and **3** (2.327(4)−2.384(4) Å) are comparable to distances observed in $[(UO_2)(Salophen)]_2$ (2.387−2.463 Å)[24] and bridged dinuclear uranyl compounds involving alkoxide (2.340−2.390 and 2.360−2.389 Å),[31,35] phenoxide (2.391−2.454 Å),[30] and solvents (methoxide and hydroxide, 2.287−2.404 Å).[45] The $U-O_{OH}$ distances in **1**−**3** (2.465(8)−2.499(4) Å) are comparable to $U-O_{solvent}$ distance reported for mononuclear $[UO_2(salpn)(MeOH/EtOH)]$ (2.463 and 2.475 Å; salpn = *N*,*N*′-propylenebis(salicylidenimine)).[29] On the other hand, these are smaller than $[UO_2(Salen)(H_2O)]$ (2.430 Å) containing water as ligating agent.[29] Hence, the terminal hydroxyl group in **1**−**3** can be considered a ligating molecule provided by the chelating ligand.

The O═U═O angles in **2** (av 177°) and **3** (178(2)°) indicate that the uranyl moiety is slightly bent compared to the angle observed in **1** (179(1)°). In **1**, the aryl groups are present on one side of the plane with a ‘cupped’ appearance (Figure 6). Such ‘cupped’ or ‘ruffled’ appearance has been reported for mononuclear uranyl complexes with salen and phenyl-based salen complexes.[24,46] This is due to the strong interaction of the ligand with the uranyl metal, which forces the ligand to conform to the coordination geometry of the metal. A similar distortion in the backbone of **2** and **3** is not observed, as the phenyl groups are present on the opposite side of the U_2O_2 plane (Figure 6). Possible reasons for this distortion include the presence of intermolecular hydrogen bonding (**2**) and steric hindrance due to the bulky *tert*-butyl groups (**3**). Despite similar distortion, the O═U═O angles in **1** are distinctly linear compared to those observed in $[UO_2(salophen)DMF/DMSO]$ (av 177°) and $[UO_2(salophen)]_2$ (av 176°). The deviation from linearity as seen in the latter compounds is due to the presence of coordinated solvent, as the angles suggest that the uranyl moiety is bent in the direction opposite to the coordinated solvent.[24]

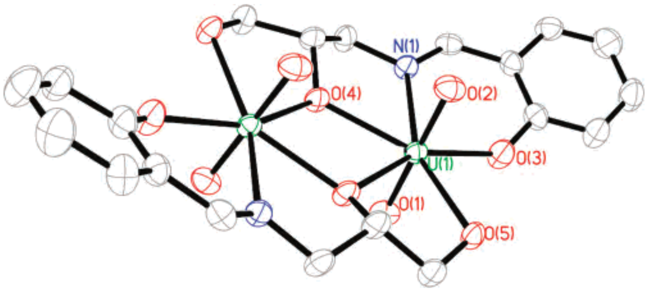

Figure 3. Molecular structure of **1** with 50% thermal ellipsoids. The solvent molecules and hydrogen atoms are omitted for clarity.

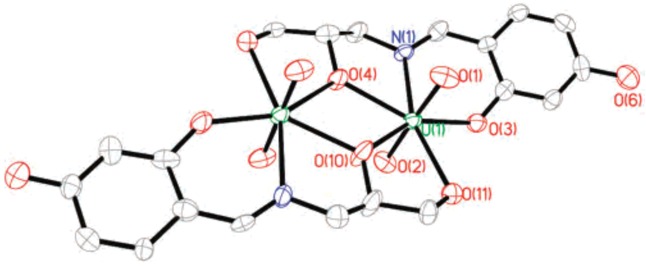

Figure 4. Molecular structure of **2** with 50% thermal ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

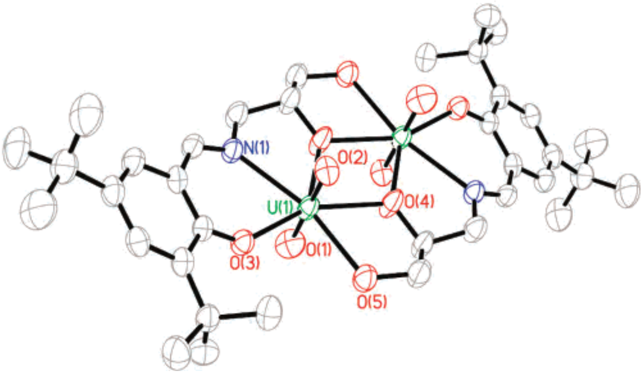

Figure 5. Molecular structure of **3** (only one unit is shown). The solvents and hydrogen atoms are omitted for clarity.

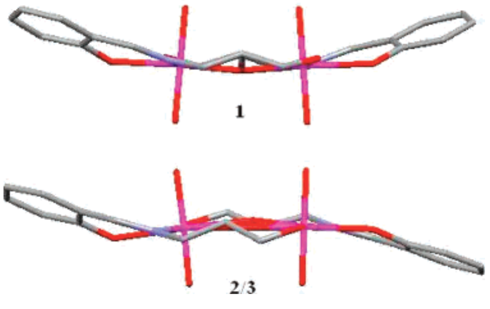

Figure 6. Distortion observed in the backbone of **1** and **2**/**3** due to electronic and steric effects.[47]

Intermolecular Interactions. The intermolecular hydrogen-bonding frameworks in the extended structure of **1** and **3**

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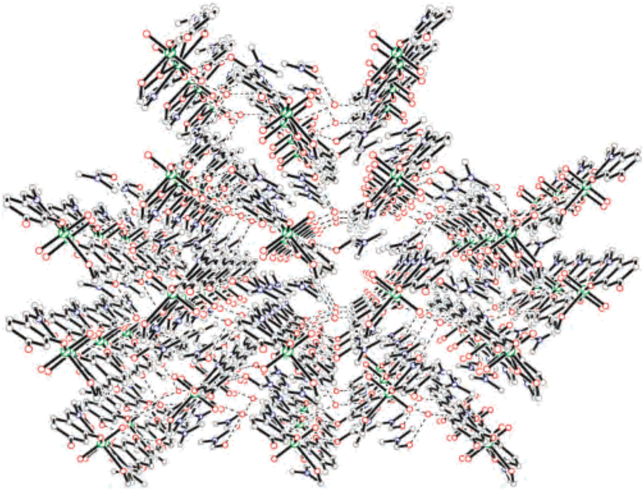

Figure 7. Lattice structure of **2** with water molecules present in the channels forming a two-dimensional framework.

are similar with hydrogen bonds observed between terminal hydroxyl groups and the solvent molecule yielding discrete molecular structures (2.614(5) and 2.596(7) Å) (Supporting Information). In compound **2**, extensive weak interactions are observed as the water molecules and hydroxyl groups present on the phenyl groups (Figure 7) interact to form an extended structure. The phenolic groups are involved in intermolecular hydrogen bonding with neighboring unit (2.730(1) Å) forming a one-dimensional chain along the *b* axis. One of the phenolic groups is also bonded to the DMF molecule (2.497(1) Å). Such unusual hydrogen bonding might be the reason for unsymmetrical U−O$_{ph}$ distances in **2**. The oxygen atoms on terminal hydroxyl group (U−O$_{OH}$) in **2** are hydrogen bonded to a water molecule (av 2.707 Å) in another direction forming a two-dimensional structure. The overall weak interactions in **2** lead to the formation of a corrugated sheet structure with the adjacent sheets perpendicular to each other.

In **1**−**3**, weak interaction of the uranyl oxygen with ‘C’ atom (attached to the adjacent terminal hydroxyl group) can be observed, where the average U═O−C distances ranges from 3.143 to 3.191 Å (C−H fixed at 0.99 Å). Similar interactions have been described in hydrated oxides of uranium (VI) (for example, [$(UO_2)_4O(OH)_6 \cdot 5H_2O$], 2.66−3.36 Å), where the uranyl oxygen are weakly associated with the water molecules present in the interlayer region.[48] The U−U distances in **1**−**3** are in the range 3.863(5)−3.932(5) Å, indicating an absence of metal−metal interaction between uranium centers.

Reactivity. A weak U−O$_{OH}$ bond and a void space present between O$_{ph}$−U−O$_{OH}$ make these compounds of particular interest for study with regard to their reactivity at the uranyl center. These compounds, however, did not demonstrate any reactivity in terms of addition or substitution reaction with added organic ligands (alkyl halides and alkyl amines) at either uranium center. Even an extended hydrogen-bonded structure with interchelated halide or amine could not be isolated. Rao et al., have shown that, with similar dinuclear complexes, no addition or substitution reaction occurs at uranium center, and the transmetallation reaction proceeds only when there exists one unbound −CH$_2$OH group.[35,49]

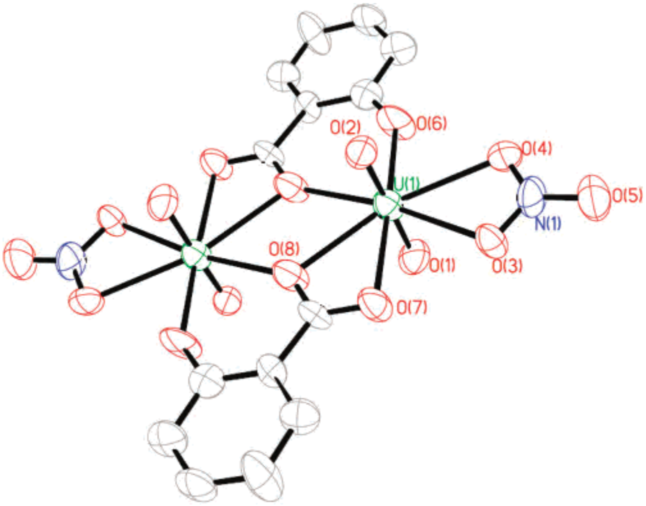

Figure 8. Molecular structure of **4**. The protonated triethylamine amine unit hydrogen bonded to O3 is not shown.

The reaction of **1** with Ag(NO$_3$) in DMF with 1 equiv of base (triethylamine) resulted in the formation of **4** (Figure 8). Hydrogen bonding between protonated triethylamine and nitrate oxygen (2.90(2) Å, 166°) suggests the presence of a cationic uranyl complex. This distance is similar to those observed between protonated triethylamine and [UO_2L_2] (2.894−2.974 Å) (L = pyridine-2,6-dicarboxylic acid).[45] The carboxylate C−O distances in **4** (1.25(2) and 1.29(2) Å) are in accordance to those observed in [$UO_2(C_6H_4OHCOO)_3$]$^-$ (**5**) (1.26−1.31 Å), indicating the presence of delocalized electrons on carboxylic groups.[50] The phenolic C−O distance of 1.29(2) Å is much smaller than the corresponding distance of C−O$_{OH}$ (1.33 Å) present on salicylic acid.[51] These make it unlikely that the proton is attached to one of these anions. Presence of bridging oxygen atom of a delocalized carboxylate group involved in the metal coordination makes **4** a unique structure, as similar bonding has not been reported for metal−salicylate complexes. The geometry around the uranyl centers is hexagonal bipyramidal, which is very similar to that observed in **5**.[50] However, the uranyl−oxygen distance (av 1.73(1) Å) in **4** is much smaller compared to that observed in **5** (av 1.77 Å). The equatorial ‘O’ atoms belonging to salicylate ion are at a distance of 2.552(1) and 2.496(1) Å. The phenolic U−O distance of 2.232(1) Å is longer than that observed in **1**−**3**. In the central U_2O_2 core, the bridging U−O distances are unsymmetrical (2.422(1) and 2.494(1) Å), as observed in **1**−**3**. The average U−O$_{Nitrate}$ distance of 2.554 Å is longer than the corresponding distance observed in [$UO_2(NO_3)_2(H_2O)_2$]·$4H_2O$ and [$UO_2(H_2L)_2(NO_3)_2$] ((2.48−2.50 Å) (L = *N*,*N*-bis(2-hydroxy-3,5-dimethylbenzyl)-2-aminoethanol).[31,52] Distortion in the backbone

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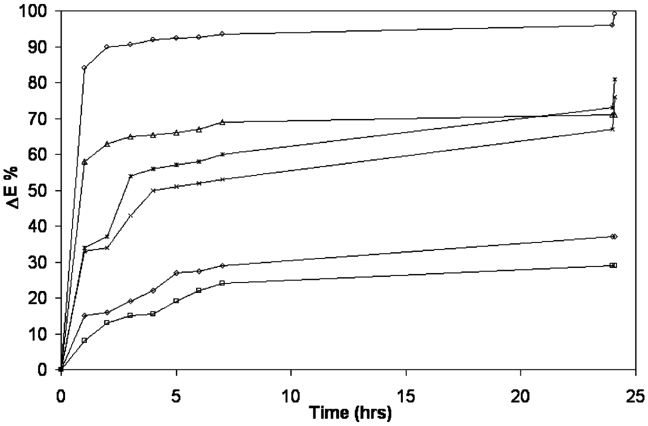

Figure 9. Graph of percent extraction of UO_2^{2+} (4×10^{-3} M) vs time at pH 3−5 in $CHCl_3$ and hexane containing H_3L3 (8×10^{-3} M) (hexane: pH 3 (□), 4 (◇), 5 (△); $CHCl_3$: pH 3 (×), 4 (*), 5 (○)).

is not observed in **4**, as the phenyl groups are coplanar to the central U_2O_2 core.

Extraction Studies. Compound H_3L3 was selected for the extraction studies due to its better solubility in hexane and chloroform (see Supporting Information for UV−vis spectrum). The stability of H_3L3 was studied at pH 1−5 in hexane and $CHCl_3$. In hexane, discoloration of the ligand was observed at pH 1 and 2, indicating dissociation of the ligand. Such discoloration was not observed in $CHCl_3$. This may be due to the presence of intermolecular hydrogen bonding in $CHCl_3$ (polarity = 4.1) compared to hexane (polarity = 0.0). Under these pH conditions, only UO_2^{2+} exists in the pH range 1−3. At pH 4−5, hydroxyl-bridged species might exist, which is evident by the extinction coefficient at higher pH.[53] Thus, at pH 4 and 5, H_3L3 can form a uranyl complex by ion exchange of H^+ of H_3L3 along with ligand exchange with bridged hydroxyl groups. A red-shift of absorption maxima in comparison to the free uranyl ion (414 nm) was observed at pH 4 (6 nm) and 5 (10 nm), which does not indicate the formation of any uranyl Schiff base complex in aqueous media.

The extraction from aqueous phase in $CHCl_3$ is much better than in hexane (Figure 9). At pH 5 in $CHCl_3$ after 1 h, a quantitative removal of UO_2^{2+} (84%) was observed compared to pH 3 and 4 samples (32% and 53%, respectively). At pH 3 after 24 h, a transfer of 29% uranyl is observed in hexane compared to 66% in $CHCl_3$. At pH 4, the corresponding values are 37% (hexane) and 70% ($CHCl_3$). At pH 5, maximum transfer is observed (72%, hexane; 97%, $CHCl_3$) due to the complete deporotonation of the hydroxyl groups of the ligand. Because of the better extraction efficiency in $CHCl_3$, an experiment utilizing 24-h constant stirring was studied. Significant extraction efficiency was observed at pH 3 and 4 (10% and 15% increment, respectively). Under similar conditions at pH 5, almost complete removal (99%) can be achieved.

Conclusion

Novel asymmetric Schiff base ligands and their uranyl complexes have been synthesized and fully characterized. The structures are similar with pentagonal bipyramidal geometry around uranyl cation and a central U_2O_2 core. The presence of different substituents on the phenyl group affects the distortion of the ligand backbone. The uranyl center is coordinated to all the available functional groups on the ligand. Unlike most of the reported uranyl complexes, a ligating solvent molecule to complete uranyl coordination is not observed in **1**−**3**. Weak intermolecular interactions involving solvent molecules, as well as uranyl oxygen atoms, yield a one-dimensional network in **1** and **3**. In **2**, the presence of an interlayer water molecule gives rise to a corrugated sheet structure. Two-phase extraction studies of uranyl ions from aqueous media at different pH conditions employing H_3L3 indicates better efficiency at higher pH (99%, pH 5).

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Supporting Information Available: Synthesis, characterization information, additional figures and packing diagram, extensive tables for bond distances and angles of **1**−**4**, hydrogen-bond geometry in **1**−**3**, crystal data, and electronic spectra of ligands and metal complexes at pH 1−5. This material is available free of charge via the Internet at http://pubs.acs.org.

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