Uranyl stabilized Schiff base complex†

Mohan S. Bharara, Stephen A. Tonks and Anne E. V. Gorden*

Uranyl Schiff base complex [(UO$_2$)$_2$(Salpro)(OH)(Solvent)$_2$] (1) in the presence of excess of ethylenediamine (EDA) does not undergo nucleophilic addition (hydrolysis) and substitution (transamination) reactions due to an extended chelation [2N, 3O + OH] by the flexible backbone.

Schiff base (SB) compounds are versatile ligands for the complexation of various metal ions and important intermediates in many enzymatic reactions.[1–3] Transamination involving the SB is a key step of biological reactions involving, for example, pyridoxal phosphate,[4] or semicarbazide-sensitive amine oxidase.[5,6] In a transamination reaction, the stronger base replaces the weaker base; in this case, the imine group (C=N) of the SB is susceptible to hydrolysis by nucleophiles.[7] Metal ion catalysis in transamination reactions of SB compounds is well documented.[8,9] With transition metal ions including Cu^{2+}, Ni^{2+}, Zn^{2+} and Fe^{2+}, the transamination reaction is equilibrium controlled, and the excess of exchanging amine favors the reaction.[7,10] Presumably, the multiple charge of the SB is more effective than the lone charge of the proton at stabilizing the carbanion formed upon heterolytic cleavage.[11] In a recent study, the uranyl ion has been demonstrated to catalyze the reversible transamination of 2-methylalanine with pyridoxal (Vitamin B$_6$), yielding [(UO$_2$PmHpyr)$_3$(μ$_3$-O)]Cl·3H$_2$O (3) (PmHpyr = pyridoxaminylpiruvate anion).[12] Transamination in uranyl-SB complexes with 8-hydroxy-7-quinolinecarbaldehyde is also reported, where the addition of EDA or diaminobenzene yields symmetrical tetradentate Schiff base complexes.[13]
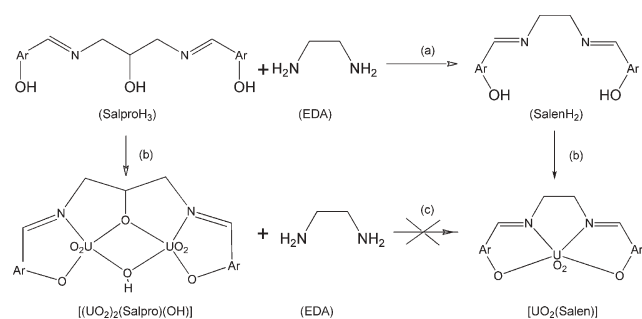
In an effort to synthesize stable uranyl-SB complexes to be used as model compounds in the investigation of new means of remediation of heavy metals from aqueous sources or nuclear wastes, we here report a dinuclear hydroxyl-bridged uranyl-SB complex, which does not undergo nucleophilic addition or substitution reactions. Recently, we have reported unsymmetrical dinuclear uranyl-SB complexes, found to be resistant to simple nucleophilic addition and/or substitution reactions.[14]

The reaction of SalproH$_3$ (1,3-bis(salicylideneamino)-2-propanol) and uranyl nitrate in the presence of an equivalent amount of triethylamine (TEA) as base in MeOH–CHCl$_3$ yielded 1·(MeOH)$_2$.‡ Similar reactions of SalproH$_3$ with metal ions such as Cu^{2+}, Mn^{3+} or Zn^{2+} typically yield multinuclear (tri-, tetra- and hexanuclear) alkoxo-bridged clusters.[15–18] Under the same reaction conditions using EDA as the base instead of TEA, the compound [UO$_2$(Salen)MeOH] (2·(MeOH)) was obtained.‡ The catalytic role

Auburn University, Auburn, AL, USA. 36849.
E-mail: gordeae@auburn.edu; Fax: 01-334-844-6959;
Tel: 01-334-844-6973
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of the uranyl ion in the transamination reaction, followed by the formation of 2·(MeOH) (similar to the formation of 3),[12] can be ruled out because in the absence of UO$_2$$^{2+}$ SalproH$_3$ undergoes facile hydrolysis and transamination with EDA to yield Salen (N,N-ethylenebis(salicylidenimine)) (Scheme 1). The reaction of 1·(MeOH)$_2$ with an excess of EDA (3 equivalents) under similar reaction conditions (heating at reflux temperature in polar solvent) failed to yield 2·(MeOH). This is probably due to blockade by the uranium atom of the protonation of the imine nitrogen atom, inhibiting the hydrolysis of the imine bond that leads to transamination.[19] Preliminary studies with uranyl-SB complexes containing [2N, 2O] coordination sites, including the uranyl-Salophen complex (Salophen = N,N-disalicylidene-o-phenylene-diamine), suggest facile transamination under mild conditions.[20]

The crystals of 1·(S)$_2$ were obtained from either DMSO or DMF and pyridine (in case of 2·(S)) from supersaturated solutions containing precipitates.§ The structures of 1·(DMF)$_2$ and 2·(Py) along with selected bond distances and angles are shown in Fig. 1 and 2, respectively. The geometry around the uranium atoms in 1·(DMF)$_2$ and 2·(Py) could be best described as pentagonal bipyrimidal with axial O=U=O moieties. In 1·(DMF)$_2$, the coordination around the metal center is completed by the imine N, aryl O, the bridging oxo-group, a bridging hydroxyl group, and a solvent molecule. The phenyl moieties are distorted and present on the opposite sides of the plane defined by the U$_2$(μ$_2$-O)(μ$_2$-OH) plane. Similar distortion has been observed in the dinuclear [UO$_2$(ASB)]$_2$ complexes (ASB = 3-amino, 1,2-propanediol based asymmetric SB ligands).[14]

The U=O distances (avg 1.786(4) Å) and O=U=O angles (avg 179(2)°) are typical of the corresponding distances and angles reported for the uranyl compounds in the literature.[21] The U–N distances (2.544(5) and 2.579(5) Å) are unsymmetrical, and in the range usually observed in uranyl-SB complexes (2.54–2.58 Å).[22] The average C=N distance in 1·(S)$_2$ (1.279(8) Å) is shorter than the

Scheme 1 Formation and reactivity of 1 (Ar = phenyl group, solvent attached to the uranyl group is not shown). Reaction steps: a: MeOH, mild conditions; b: UO$_2$$^{2+}$ and triethylamine; c: reflux with excess EDA.
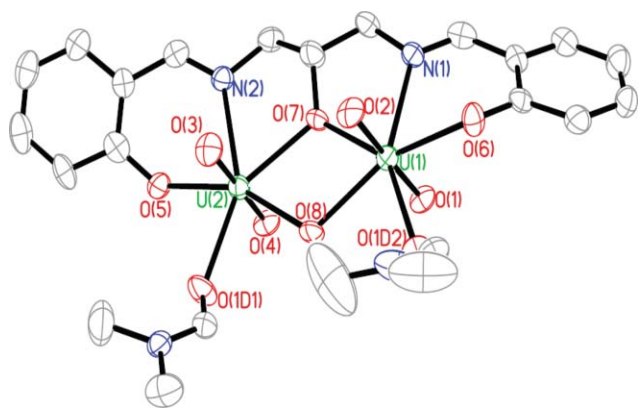
Fig. 1 Molecular structure of **1·(DMF)₂** (ORTEP drawing with 50% thermal ellipsoids). The selected bond distances (Å) and angles (°) are U1–O1, 1.792(4); U1–O2, 1.783(4); U1–O6, 2.241(5); U1–O7, 2.380(5); U1–O8, 2.327(4); U1–O1D2, 2.461(5); U1–N1, 2.544(5); U1–U2, 3.869(8); O1–U1–O2, 178.7(2).
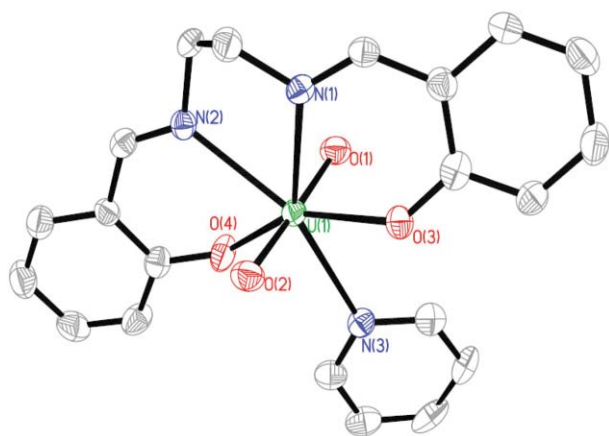

Fig. 2 Molecular structure of **2·Py** (ORTEP drawing with 50% thermal ellipsoids). The selected bond distances (Å) and angles (°) are U1–O1, 1.783(4); U1–O3, 2.242(4); U1–O4, 2.230(3); U1–N1, 2.544(5); U1–N3, 2.617(6); O1–U1–O2, 177.3(2).

corresponding distances observed in [UO₂(Salophen)(S)] (S = MeOH (1.30 Å), DMF (1.289 Å), and DMSO (1.290 Å)).[22,23] The presence of a stronger C=N bond, which is most probably due to the flexible backbone resulting in better chelation around the metal ion, might explain its inhibition toward hydrolysis.

The bridging oxo distances (avg U–O7 = 2.372(4) Å) are in accordance with the U–O_{oxo} distances observed in [UO₂(Salophen)]₂ (2.387–2.463 Å)[22] and [(UO₂)(H₂L)₂(NO₃)] (2.360–2.389 Å)[24] (H₂L = aminoalcoholbis(phenolate)). The U–OH distances (2.327(4) Å and 2.342(4) Å) are unsymmetrical and much shorter compared to the U–O_{oxo} distances, indicating stronger bonds. These distances are in agreement with the corresponding distances observed in uranyl-oxalate complex, [(UO₂)₂(C₂O₄)₂(OH)Na(H₂O)₂] (avg 2.287 Å);[25] uranyl-pyridine-2,6-dicarboxylato complex, [HNEt₃]₂[UO₂L₂]·2H₂O (2.319–2.357 Å);[26] as well as uranyl-inorganic frameworks such as [(UO₂)₄O(OH)₆]·5H₂O (2.303–2.433 Å).[27]

The structure of **2·(S)** with H₂O, EtOH, or DMSO as coordinating solvent has been described in detail;[28] however, a

few discrepancies in the bond distances between **2·(Py)** and **2·(H₂O/EtOH/DMSO)** and similar uranyl-SB (with Py as coordinating solvent) have been observed. For instance, the average U–O distance in **2·(Py)** (2.236(3) Å) is smaller than those reported for **2·(H₂O/EtOH/DMSO)** (avg 2.281, 2.267 and 2.248 Å, respectively).[28] Similarly, the U–N_{py} distance in **2·(Py)** (2.617(6) Å) is shorter than those observed in [UO₂(*tert*-butylSalen)(Py)] (2.640 Å) and [UO₂(Salpn)(Py)] (2.632 Å) (Salpn = *N,N*-propylenebis(salicylidenimine)).[28] The O=U=O angle and U–N distances are, however, within the range observed in these cases.[28]

In conclusion, we have synthesized a novel dinuclear uranyl-SB complex (**1·(S)₂**), which does not undergo nucleophilic addition and substitution reactions, contrary to SB complexes with transition metal ions. The extended chelation due to the flexible backbone as well as the bridging hydroxyl group provides stability to the overall complex. Such compound(s) could be useful to further explore the uranium chemistry from remediation as well as speciation points of view. This may also be of interest in stabilizing wastes from nuclear fuel sources in alkaline solutions. We are continuing with the investigation of similar reactivity with different uranyl-SB complexes with variable or extended backbones.
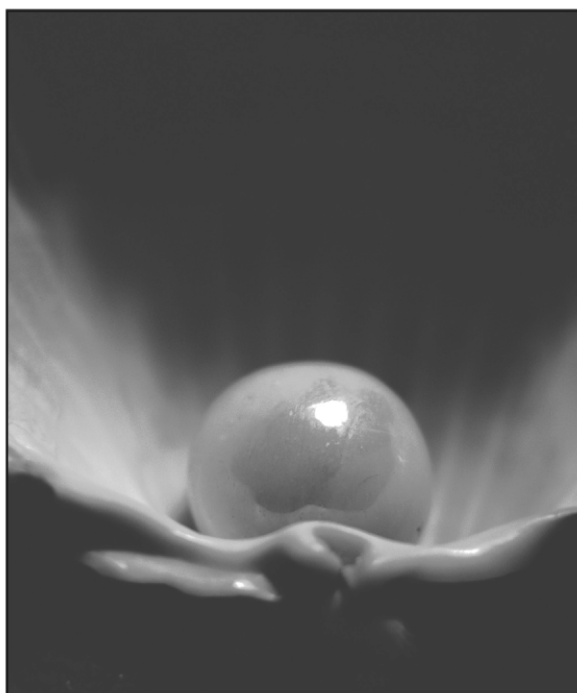
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20 Further studies with various uranyl-Schiff base complexes are underway.

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