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# En Route Activity of Hydration Water Allied with Uranyl ($UO_2^{2+}$) Salts Amid Complexation Reactions with an Organothio-Based (O, N, S) Donor Base

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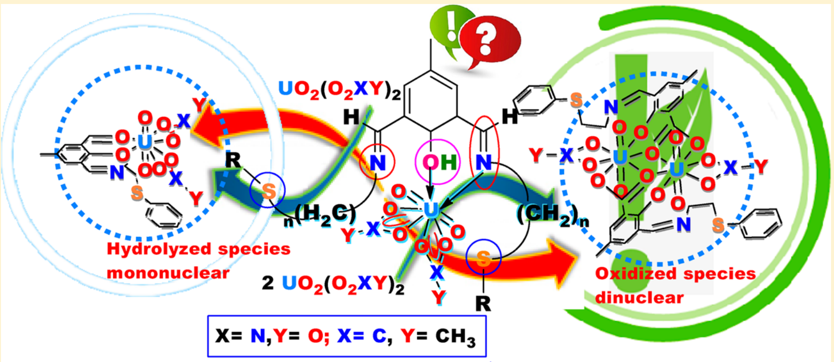
Supporting Information



**ABSTRACT:** This study provides en route activity of hydration water allied with uranyl salts amid complexation reactions with a donor species **L** bearing O, N, and S (phenolic, −OH; imine, −HC═N−; and thio-, −S−) donor functionalities. The $UO_2^{2+}$/**L** reaction encounters a series of hydrolytic steps with hydration water released from uranyl salts during the complexation processes. Primarily, the coordinated $[L_{(-HC=N)(OH)(-HC=N)} \rightarrow UO_2(NO_3)_2/(OAc)_2]$ species formed during the complexation process undergoes partial hydrolysis of the coordinated ligand resulting in the isolation of an aldehyde coordinated uranyl species $[\mathbf{L}_{(-HC=N)(OH)(-HC=O)} \rightarrow UO_2(NO_3)_2/(OAc)_2]$. The influence of hydration water continued as the reaction further proceeded to the next stage resulting in alteration of the aldehyde coordinated uranyl species $[\mathbf{L}_{(-HC=N)(OH)(-HC=O)} \rightarrow UO_2(NO_3)_2/(OAc)_2]$ to an oxidized carboxy coordinated uranyl species $[\mathbf{L}_{(-HC=N)\ (OH)\{-C(=O)O\}} \rightarrow (NO_3)/(OAc)]_2$ without the use of any external oxidizing agents. These studies are of particular significance as they allow one to realize the adventitious role of hydration water released from commonly used uranyl salts during their reaction with organic donor substrates in nonaqueous medium. These results also form an experimental basis to understand the critical behavior of $UO_2^{2+}$ ion activity (as oxidizing, reducing, or catalytic) relevant in many chemical, biological, and environmental processes.

## ■ INTRODUCTION

An understanding of the behavior of the $UO_2^{2+}$ ion among the actinides has been the subject of particular attention due to increasing global *nuclear energy demand*.[1] As a consequence, their presence in nature also poses serious environmental concerns where they may come across a myriad of chemical, geochemical, biochemical, and environmental processes.[2] Naturally, the knowledge of the behavior of cationic $UO_2^{2+}$ is a prerequisite for a precise monitoring, speciation, and furthermore their interactions during migration within terrestrial humic substances.[3] Basically, humic substances have been considered as possible remediation strategies in safe nuclear waste alteration and reprocessing of nuclear fuel sources.[4] Although the interactive behavior of the $UO_2^{2+}$ ion toward humic substances is well documented, uncertainties remain due to the structural complexities that vary as a function of pH or as a function of metal ion concentration.[5] Similarly, intricate reaction dynamics of the $UO_2^{2+}$ ion that normally go by an oxidative−reductive process in aqueous or organic solutions result in structural diversities, and therefore, there is always uncertainty in their actual speciation and geochemical migration. For example, U(VI) has a strong tendency to hydrolyze and support a range of oxo- and hydroxo- species ($mUO_2^{2+} + nH_2O \rightleftharpoons (UO_2)_m(OH)_n^{(2m-n)} + nH^+$, where the $n$ and $m$ range is 1−5 or 1−9) in aqueous medium.[6] There is also a bias to the hydrolysis reaction of the $UO_2^{2+}$ ion in different environments (acidic or basic conditions as well as aerobic and anaerobic environments) as $H^+$ and $OH^-$ ions are freed from hydrolytic activity of $UO_2^{2+}$ ion through their biotic and abiotic interactions. This further leads to substantial uncertainties about speciation of the uranyl ion in a similar environment as different species and several coexisting polymeric species at similar concentration and pH range may be produced.[7] Nevertheless, an understanding of the behavior of the $UO_2^{2+}$ ion in diverse environments is

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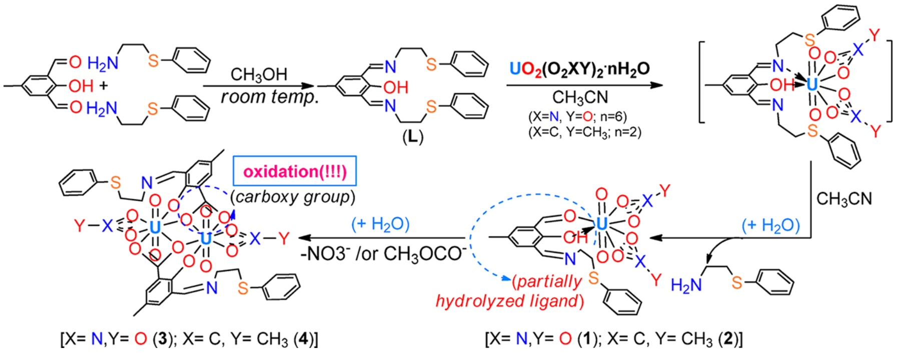
Scheme 1. Synthesis of O, N, S-Based Donor Species L and Its Reactions with $UO_2^{2+}$ Salts



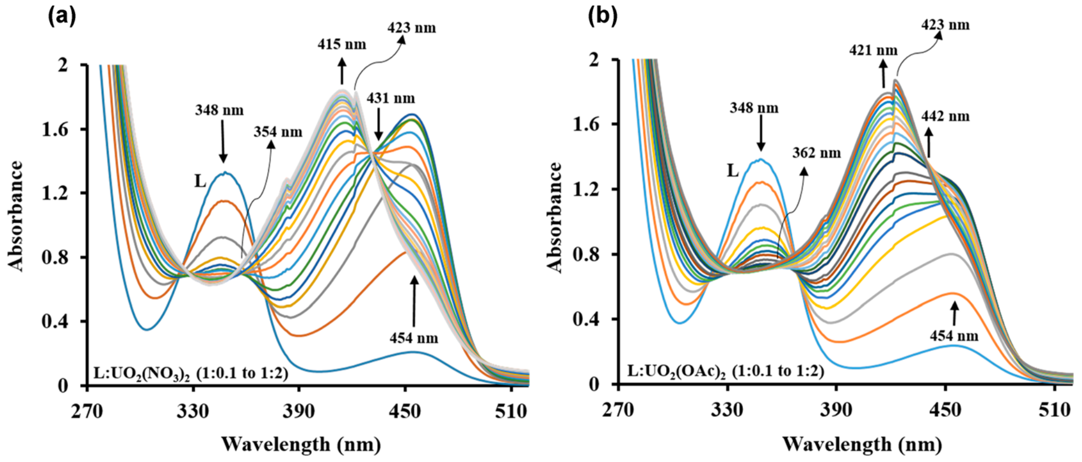


**Figure 1.** Spectrophotometric UV−Vis titrations: (a) spectroscopic changes titrating the **L** ($1 \times 10^{-4}$ M) with $UO_2(NO_3)_2{\cdot}6H_2O$ ($1 \times 10^{-3}$ M) in acetonitrile, (b) spectroscopic changes titrating the **L** ($1\times 10^{-4}$ M) with $UO_2(OCOCH_3)_2{\cdot}2H_2O$ ($1 \times 10^{-3}$ M) in acetonitrile.

considered very essential in order to infer their precise speciation and remediation. Therefore, the pursuit of any new knowledge is fundamental to the advancement of $UO_2^{2+}$ chemistry,[8] and this can realized through the use of variable donor species[9] or well-structured organic species with heteroatomic donor combinations. Indeed, the outcome of their combinations with the $UO_2^{2+}$ ion may allow further promoting and understanding structure−property relationships. These studies could offer practical advantages compared to their individual donor analogues in terms of their discriminatory functions. Our group also initiated this line of research by investigating cyclic organic species bearing heteroatomic (O, N, X) (X = S, Se, or Te) donor combinations. Such species exhibited a selective binding affinity for $UO_2^{2+}$ ions over a variety of transition and heavy metal ions including alkali and alkaline-earth metal ions.[10]

Considering further new application of the chalcogen related species in $UO_2^{2+}$ chemistry and their functional behavior,[9] we recognized and came across an essentially useful acyclic donor species **L** bearing an O, N, S donor combination to examine the behavior of the $UO_2^{2+}$ ion. The donor species **L** bearing phenolic (−OH), imine (−HC═N−), and thio- (−S−), a Schiff base type donor, is an obvious choice to study its chemistry with uranyl ions. Besides heteroatomic characteristics, S···heteroatom(s) interactions may also provide the donor species as well as their complexes an additional intrinsic chemical stability to overcome the difficulty associated with this kind of species, which are often prone to hydrolysis. Apparently, this study may also be interesting with the view that contamination of $UO_2^{2+}$ in groundwater is a serious environmental concern and many enzyme catalytic sites in biological systems frequently embrace nitrogen or/and sulfur as coordination sites. Interestingly, the ligand **L** bears donor sites usually present in humic substances. Usually humic substances contain a variety of phenolic-, carboxylic-, or even enolic donor functionalities and are widely distributed in soils, sediments, oceans, and fresh and ground waters.

## ■ RESULTS AND DISCUSSION

The donor species **L** was obtained by the condensation reaction of 2,6-diformyl-4-methylphenol with phenylthioethylamine and was found to be enough stable toward atmospheric air in ambient laboratory conditions. The outline of the synthetic procedure for ligand synthesis and their successive complexation reactions with uranyl ion is shown in Scheme 1.

In order to understand the interactive behavior of **L** with metal ions, metal/ligand titration experiments were performed and monitored by UV−vis spectroscopic changes. Remarkably, the spectral changes on addition of the $UO_2^{2+}$ ion as $UO_2(NO_3)_2{\cdot}6H_2O$ or $UO_2(OCOCH_3)_2{\cdot}2H_2O$ to a solution of **L** was special compared to those observed for other hydrated metal cations (Figure S1). In spectroscopic measurements, on gradual addition of a solution of the $UO_2^{2+}$ ion to a solution of **L** in acetonitrile, a significant blue shift was exhibited when $UO_2^{2+}$:**L** concentrations reached to a molar ratio of 0.6:1 and continued up to a molar ratio of 2:1 (Figure 1). The appearance of two isosbestic points at 431 and 354 nm for $UO_2(NO_3)_2{\cdot}6H_2O$ and 442 and 362 nm for

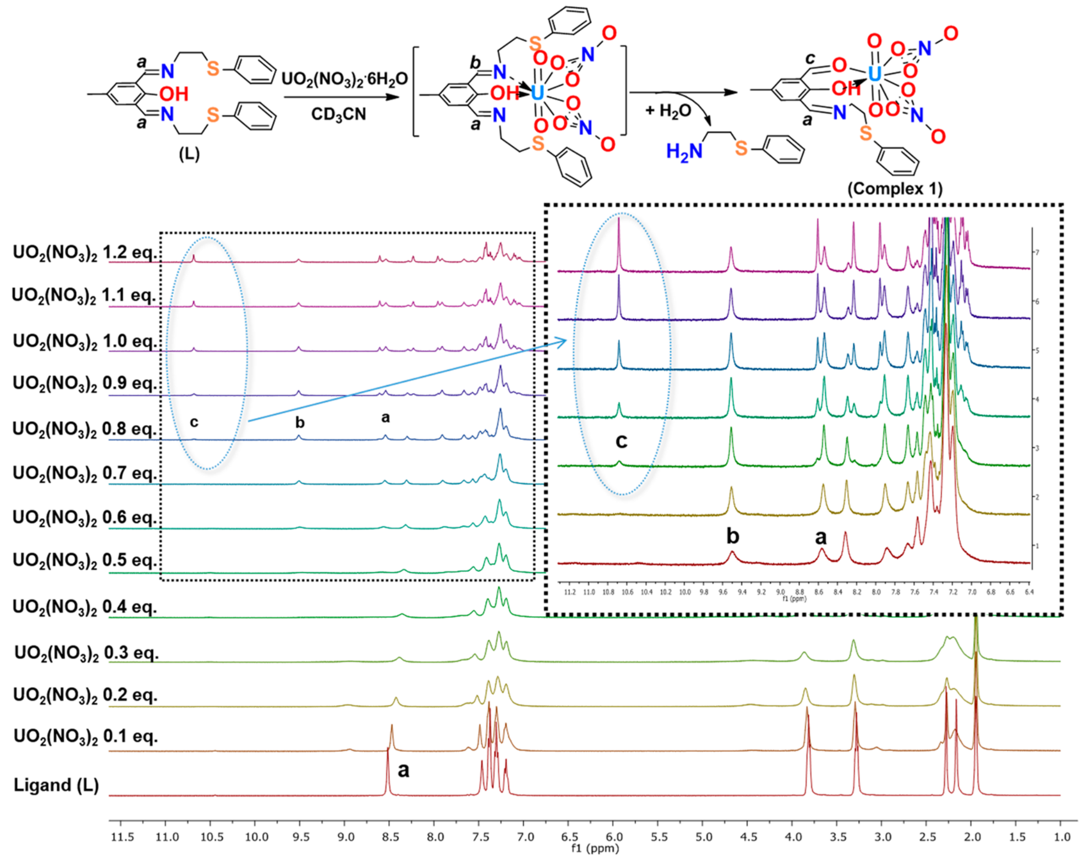


**Figure 2.** Changes observed in $^1H$ NMR spectroscopy on titrating the **L** with $UO_2(NO_3)_2{\cdot}6H_2O$ in $CD_3CN$ (up to L:$UO_2^{2+}$ ratio reached 1:0.1 to 1:1.2). (inset) Peak "a" corresponding to imine proton ($-H_aC{=}N$) of **L**, appearance of new peaks "b" corresponding to coordinated imine proton ($-H_bC{=}N$) and "c" ($-H_cC{=}O$) as a consequence of in situ hydrolysis of coordinated species.

$UO_2(OCOCH_3)_2{\cdot}2H_2O$ in UV−vis spectra as a function of the added $UO_2^{2+}$ ion was found to be consistent and reproducible upon repeated experimentation. Nevertheless, these results reveal an intricate solution behavior, where possibilities of competition between solvation ($CH_3CN$ or $CH_3OH$) vs desolvation, hydration/hydrolysis, complexation followed by hydrolysis, partial or complete hydrolysis of ligand (L) or metal salts, and deprotonation of the phenolic (−OH) of ligand are likely to occur. Therefore, a real picture of $UO_2^{2+}$−ligand interactions in organic solvent may not be directly precise, especially when speciation of the $UO_2^{2+}$ ion is passing through a series of parallel reactions with respect to other metal cations.

The $^1H$ NMR spectroscopic titration studies of **L** with $UO_2(NO_3)_2{\cdot}6H_2O$ or $UO_2(OCOCH_3)_2{\cdot}2H_2O$ in $CD_3CN$ provide a rather reasonable picture of the $UO_2^{2+}$ ion binding to some extent and also its post consequences. In representative $^1H$ NMR experiments, on adding small aliquots of $UO_2^{2+}$ solution (a solution of $UO_2(NO_3)_2{\cdot}6H_2O$ in $CD_3CN$) to a solution of **L** (in $CD_3CN$) revealed the appearance of two types of $-HC{=}N$ protons, where one of them coordinates to the $UO_2^{2+}$ ion via its −N donor center. The coordinated imine proton ($-H_bC{=}N$) was assigned to 9.53 ppm. As the concentration of the $UO_2^{2+}$ ion increased, the spectral changes continued along with the appearance of the aldehyde ($-H_cC{=}O$) proton signal at $\delta$ 10.68 ppm (Figure 2). Similar spectral changes in the $^1H$ NMR spectroscopic measurements were also seen when a solution of $UO_2(OCOCH_3)_2{\cdot}2H_2O$ (in $CD_3CN$) was used for titration with **L** (Figures S5 and S6). The formation of −CHO functionality might result as a consequence of partial hydrolysis of coordinated imine linkage hydrolyzed due to released hydration water associated with uranyl salts. The hydrolysis aspect may not be very unexpected; however, the partially hydrolyzed ligand species appeared to remain coordinated to the $UO_2^{2+}$ ion through its hydrolytically evolved aldehyde ($-HC{=}O$) function.

The formation of possible uranyl species was experiential and therefore determining the exact nature and geometry of these species could reveal precise speciation. In this regard, a series of experiments were carried out where, a mixed ($UO_2^{2+}$:L) solution in acetonitrile in varied molar concentrations (in molar fraction from 0.2:1 to 1:2) under ambient conditions were used to obtain their crystals. Upon repeated attempts, suitable crystal from a solution of combination of $UO_2(NO_3)_2{\cdot}6H_2O$ and **L** (1:1) in acetonitrile was obtained and analyzed by single-crystal X-ray diffraction analysis.

The perspective view of the complex **1** (space group $P21/c$) is shown in Figure 3. In the crystal structure of the species **1**, the $UO_2^{2+}$ ion was found to be coordinated with aldehyde oxygen ($-HC{=}O$) and phenolic (−OH) as donor atoms of a partially hydrolyzed ligand with (U−O) bond distances of 2.442(3) and 2.337(3) Å, respectively. The U−O bond distances for [O═U═O] are 1.738(4) and 1.733(5) Å with a bond angle of 178.0(2)°. The nitrate anions were found to be coordinated to the $UO_2^{2+}$ ion in nearly symmetrical bidentate chelation mode. The U−O ($U{-}ONO_2$) bond distances were found in the range between 2.519(4) and 2.491(3) Å and thus

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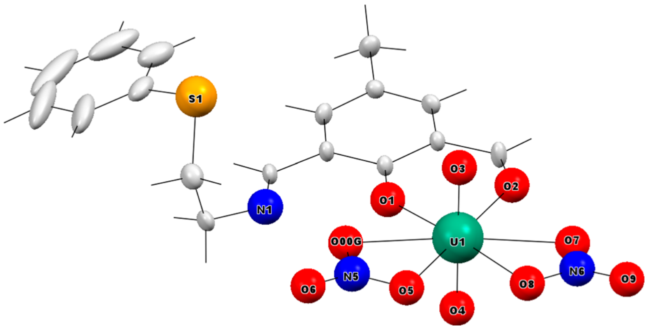

**Figure 3.** Perspective view of the partially hydrolyzed uranyl complex **1** $[\mathbf{L}_{(-\mathrm{HC{=}N})(\mathrm{OH})(-\mathrm{HC{=}O})} \rightarrow \mathrm{UO_2(NO_3)_2}]$.

providing a hexagonal−bipyramidal coordination environment to the $UO_2^{2+}$ ion.

Curiously, crystal structures obtained from a combination of hydrated uranyl salts $[\mathrm{UO_2(NO_3)_2{\cdot}6H_2O}$ or $\mathrm{UO_2(OCOCH_3)_2{\cdot}2H_2O})]$ with **L** in molar concentration (1.2:1) in acetonitrile at room temperature were also desirable as changes in UV−vis spectra of **L** in acetonitrile with increased concentration of $UO_2^{2+}$ ions were noticeable. The complex species **3** and **4** were crystallized in the space group *P*21/*c*, and perspective views of complex species **3** and **4** are shown respectively in Figures 4 and 5.

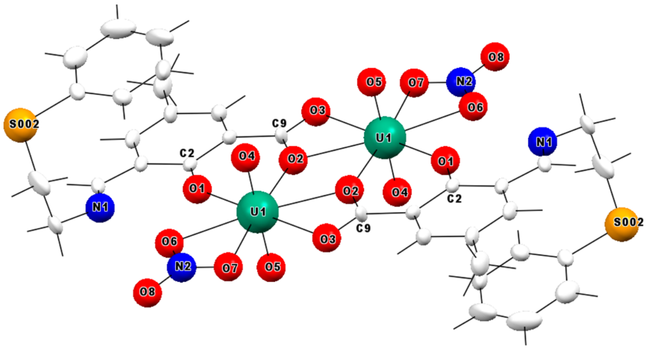

**Figure 4.** Perspective view of species $\mathbf{3}[\mathbf{L}_{(-\mathrm{HC{=}N})(\mathrm{OH})(\mathrm{COO})} \rightarrow \mathrm{UO_2(NO_3)}]_2$ as dinuclear uranyl species.

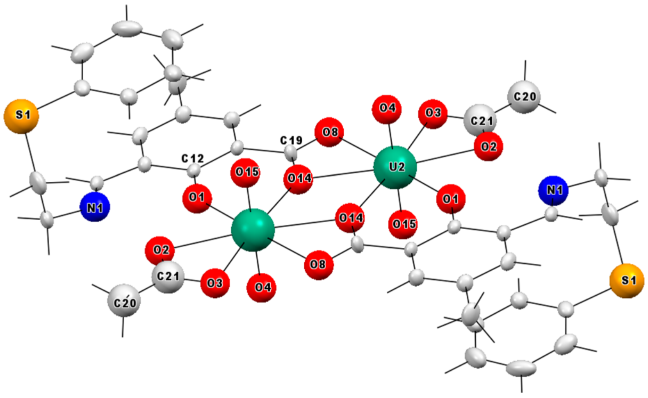

**Figure 5.** Perspective view of species **4** $[\mathbf{L}_{(-\mathrm{HC{=}N})(\mathrm{OH})(\mathrm{COO})} \rightarrow \mathrm{UO_2(OCOCH_3)}]_2$ as a dinuclear uranyl species.

Complex species **3** that resulted as a conversion of CHO → $COO^-$ further binds to the uranyl ion with (U−O) bond distances of 2.442(5) Å and to another uranyl ion in bidentate chelation mode with (U−O) bond distances of 2.481(5) and 2.534(5) Å. The newly generated carboxylate functionality, in fact, acts as both bridging as well as bidentate chelating donors between two uranyl ions and providing nearly a symmetrical dinuclear structure to two $UO_2^{2+}$ ions with a U···U separation of 4.2728(5) Å. The binding of phenolic −OH with a (U−O) bond length of 2.331(5) Å was similar as seen in **1**. The remaining coordination environment around each uranyl ion was completed with the help of one of the nitrate ions bonded to each side of the $UO_2^{2+}$ ion in bidentate chelation mode. The crystal structure data of the complex species **3** further allowed us to realize the alteration of complex species **1** → **3**, i.e., $[\mathbf{L}_{(-\mathrm{HC{=}N})(\mathrm{OH})(-\mathrm{HC{=}O})} \rightarrow \mathrm{UO_2(NO_3)_2}]$ to $[\mathbf{L}_{(-\mathrm{HC{=}N})\,(\mathrm{OH})\{-\mathrm{C}(=\mathrm{O})\mathrm{O}\}} \rightarrow \mathrm{UO_2(NO_3)}]_2$ (**1** → **3**).

Therefore, the behavior of the $UO_2^{2+}$ ion with the acetate ion further allowed us to examine the crystal studies for complex **4**. The complex species **4** also showed similar bonding patterns and geometrical arrangement around the uranyl ion as were seen in complex **3** (Figure 4). It is evident from a comparison of all three structures (species **1**, **3**, and **4**) that the $UO_2^{2+}$ ion is confined in similar geometrical arrangements, i.e., a hexagonal−bipyramidal coordination environment. Further, nearly identical U−O bond distances $(\mathrm{U{-}OH_{(phenolic)}})$ of 2.341(3), 2.331(5), and 2.328(3) Å and C−O bond distances $(\mathrm{C{-}OH_{(phenolic)}})$ of 1.294(5), 1.303(8), and 1.315(6) Å were observed in species **1**, **3**, and **4**, respectively. The U−O bond distances were found slightly longer than those observed in a number of uranyl complexes (usually in range of 2.231−2.296 Å) obtained from deprotonated Schiff bases resulting from 2,6-diformylphenol derivatives. Similarly the C−O bond distances were found to be similar in range as seen for free Schiff bases or their metal complexes in non-deprotonated form.[11]

Structurally, the donor species appeared to be symmetrical in nature as the $^1$H NMR spectrum obtained in $CDCl_3$ or $CD_3CN$ showed desired resonances for species **L** with expected multiplicity. The donor species was also found to be enough stable toward other hydrated metal cations and barely showed any hydrolysis of imine (C═N) linkage except during its reactivity with the $UO_2^{2+}$ ion. The **L** also forms complexes with other metal cations in their hydrated forms, and no hydrolytic activity on the donor base was seen. Besides, deprotonation of the phenolic proton on association with other metal cations was also not seen in current reaction conditions. Nevertheless, the complex species **1** crystallized out from an acetonitrile solution as a partially hydrolyzed species $[\mathbf{L}_{(-\mathrm{HC{=}N})(\mathrm{OH})(-\mathrm{HC{=}O})} \rightarrow \mathrm{UO_2(NO_3)_2}]$ confirmed unequal reactivity of the two azomethine substituted thio-donor arms of **L** toward $UO_2^{2+}$ ions. The uranyl coordinated azomethine group undergoes a hydrolytic reaction caused by released hydrated water from starting materials resulting in the formation of aldehydo-coordinated species **1** or **2** and parting the other azomethine (−HC═N−) donor arm away from coordination. It is interesting to note that at this stage of reaction, hydrolysis of the coordinating uranyl part was not seen. On moving from speciation of **1** or **2** to further **3** and **4**, the present findings suggest that there is no deprotonation of phenolic proton of **L** in the presence of $UO_2^{2+}$ ion in methanol or acetonitrile. The astonishing issue, which is hard to ignore, is alteration of $[\mathbf{L}_{(-\mathrm{HC{=}N})(\mathrm{OH})(-\mathrm{HC{=}N})} \rightarrow \mathrm{UO_2(NO_3)_2/(OAc)_2}]$ (complexes **1** or **2**) to oxidized species $[\mathbf{L}_{(-\mathrm{HC{=}N})(\mathrm{OH})(-\mathrm{COO})} \rightarrow \mathrm{UO_2(NO_3)/(OAc)}]_2$ (complexes **3** or **4**), i.e., conversion of −CHO to $-COO^-$ donor functionalities without use of any external oxidizing agents. In general, binding of uranyl ions with carboxylate functionality is seen in enzymes and humic substances.[12] Basically, humic substances have been considered as a possible way to alter $UO_2^{2+}$ and retard its biogeochemical migration under abiotic and biotic conditions.[13] A correlation of spectroscopic observations with those of single crystal X-ray studies of **1**, **3** and **4** allows one to remark on the chemical pathways for the conversion of −CHO to $-COO^-$ functionality. Normally, complexes comprising uranyl-Schiff bases with the C═N bond are relatively stable in organic solvents *albeit* little bit susceptible to hydrolysis under acidic conditions. Hydrolysis of coordinated **L** in present case may be suggested to involve a carbinolamine [−NH−CH(OH)−] intermediate, formed by the addition of released water to the imine linkage followed by C−N bond cleavage in the N protonated form. Further, the possible chemical conversion of −CHO to −COOH is likely to happen only under oxidative conditions either when oxidizing agents are added or possible oxidizing substrates were formed during the reaction. We further point out that formation of peroxouranyl species from $UO_2^{2+}$ has also been suggested under photolytic and nonphotolytic conditions in aqueous medium.[14] Mostly these reports suggest that the peroxide formation occurs due to water oxidation by a light generated excited $*U(VI)O_2^{2+}$ species to yield $H_2O_2$ and the reduced uranyl species $U(V)O_2^+$ that is consequently reoxidized by $O_2$ or may disproportionate to yield $U(VI)O_2^{2+}$ and insoluble U(IV) species.[15−17]

Complex species **1** or **2** were found to be enough stable when left open for weeks to atmospheric air in ambient laboratory conditions and even recovered unaltered from their solutions in methanol or acetonitrile. We also could not find any other genuine experimental reason in our reaction conditions to support formation of $H_2O_2$ or interference of atmospheric oxygen that can lead to the conversion of uranyl coordinated −CHO [$\mathbf{L}_{(-HC=N)(OH)(-HC=O)} \rightarrow UO_2(NO_3)_2/(OAc)_2$] (complexes **1** or **2**) to −COO [$\mathbf{L}_{(-HC=N)\,(OH)\{-C(=O)O\}} \rightarrow (NO_3)/(OAc)]_2$ (complexes **3** or **4**) functionality. We considered all possible experimental factors[15−18] and reasoned that the formation of species **3** and **4** comes into view as a result of further hydrolytic activity of **1** and **2** in a reaction mixture with increasing $UO_2^{2+}$ solution. This may have possibly proceeded as en route activity of hydration water. Considering possible ways of oxidation in uranyl chemistry, we propose the conversion of [$\mathbf{L}_{(-HC=N)(OH)(-HC=O)} \rightarrow UO_2(NO_3)_2/(OAc)_2$] to [$\mathbf{L}_{(-HC=N)\,(OH)\{-C(=O)O\}} \rightarrow UO_2(NO_3)/(OAc)]_2$ resulted from partially hydrolyzed species **1** or **2** which further got hydrolyzed as only one of the anion bound to uranyl ion was seen resulting in dinuclear complexes. This hydrolysis may have further led to the formation of a reactive intermediate species, where the uranyl bonded aldehyde group may accommodate a positive charge followed by a charge balancing −OH group in place of the liberated anion. The positively charged carbon of coordinated −CHO may be possibly further stabilized by the −OH group bonded to the uranyl ion. This situation may allow reduction of U(VI) species to U(V) followed by hydration of the aldehyde group. The released anion ($NO_3^-$ or $CH_3OCO^-$) might act as a base and abstract the $H^+$ from the coordinated hydrated aldehyde site to give donor carboxylate functionality and recurring uranyl(V) species back to its original oxidation state U(VI) through dimerization as seen by the formation of species **3** or **4**.

## CONCLUSIONS

The present study is of particular interest as it targets the use of O, N, S-based organic donors in understanding uranyl chemistry under nonaqueous conditions. The donor combinations of ligand species provide opportunities in understanding the hidden behavior of the uranyl ion that would not have been possible to observe in aqueous medium. The present study is of particular curiosity that allows one to realize the adventitious role of hydration water, normally associated with analytically used uranyl salts, which influences the reactivity of $UO_2^{2+}$ ion through its en route activity. These results also form an experimental basis in viewing the critical behavior of $UO_2^{2+}$ ion activity (as oxidizing, reducing, or catalytic) and may be relevant to many chemical, biological, and environmental processes especially in their biogeochemical migration.

## EXPERIMENTAL SECTION

***Caution!*** *Uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ and uranyl acetate $UO_2(OCOCH_3)_2 \cdot 2H_2O$ principally containing the isotope ($^{238}U$) are reportedly radioactive materials and must be handled in dedicated fume hoods or glove boxes with a proper facility for their disposal. Any solid waste (such as gloves) can be disposed of as ordinary waste, unless heavily contaminated.*

**Synthesis of Ligand (L).** To a stirred solution of 2,6-diformyl-4-methylphenol (0.25 g, 1.0 mmol) in dry methanol (20 mL) 2-phenylthioethylamine (2.0 mmol) in dry methanol (20 mL) was added dropwise, and the reaction mixture was allowed to stir at room temperature for 4−5 h under dinitrogen atmosphere. After completion of the reaction, the solvent was evaporated under reduced pressure, which gave ligand as a yellow solid that was pure enough for further reactions.

$C_{25}H_{26}N_2OS_2$ (**L**) Yield: 85%; mp 60 °C; IR (KBr pellet): $\nu$ (in $cm^{-1}$) 3727, 3445, 3056, 2924, 2855, 2360, 1636, 1596, 1532, 1457, 1368, 1033, 971, 840, 739, 688, 490; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm): 8.48 (s, 2H), 7.41−7.38 (m, 4H), 7.35 (s, 2H), 7.29−7.24 (m, 4H), 7.19−7.14 (m, 2H), 3.82 (t, 4H), $J$ = 6.6 Hz), 3.23 (t, 4H, $J$ = 6.6 Hz), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm): 159.2, 135.7, 132.7, 129.7, 129.1, 127.6, 126.3, 121.0, 59.6, 34.6, 20.3; ES-MS: 435.1532 $[M + H]^+$; Anal. Calcd. for $C_{25}H_{26}N_2OS_2$: C, 69.09; H, 6.03; N, 6.45; Found: C, 69.32; H, 5.98; N, 6.98.

**Synthesis of $UO_2$(VI) Complex (1).** A solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (1.0 mmol) in acetonitrile (2 mL) was added to a solution of **L** (1.0 mmol) in acetonitrile (8 mL), and instantly the solution turned red from yellow and was kept stirring overnight. The reaction mixture was concentrated under reduced pressure, and the resulting viscous mass was washed with diethyl ether; the obtained precipitate was dried and dissolved in acetonitrile and kept for crystallization, and after a few days red crystals were obtained suitable for X-ray analysis. mp 180−184 °C, Anal. Calcd. for $C_{17}H_{16}N_3O_{10}SU$: C, 29.49; H, 2.33; N, 6.07; Found: C, 29.38; H, 2.28; N, 5.96; IR (KBr pellet): $\nu$ (in $cm^{-1}$) 3492, 3430, 3245, 3165, 3019, 2932, 2853, 2353, 1660, 1629, 1528, 1437, 1382, 1281, 1193, 1130, 1037, 939, 876, 828, 745, 683, 563, 509.

**Synthesis of $UO_2$(VI) Complex (2).** Complex **2** was synthesized in identical manner as complex **1**. A solution of $UO_2(OAc)_2 \cdot 2H_2O$ (1.0 mmol) in acetonitrile (2 mL) was added to a solution of **L** (1.0 mmol) in acetonitrile (8 mL). Suitable yellow crystals obtained for X-ray analysis. mp 185−189 °C, Anal. Calcd. for $C_{21}H_{24}NO_8SU$: C, 36.63; H, 3.51; N, 2.03; Found: C, 36.56; H, 3.49; N, 1.98; IR (KBr pellet): $\nu$ (in $cm^{-1}$) 3787, 3616, 3163, 3004, 2944, 2357, 2292, 2252, 1826, 1635, 1441, 1376, 1038, 918, 748, 693, 552, 477, 434.

**Synthesis of $UO_2$(VI) Complex (3).** A solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (1.2 mmol) in acetonitrile (2 mL) was added to a solution of **L** (1.0 mmol) in acetonitrile (8 mL); instantly solution turned to red from yellow and was kept stirring in the dark overnight. The reaction mixture was concentrated to evaporate the solvent, resulting viscous mass was washed with diethyl ether, and the obtained precipitate was dried and dissolved in acetonitrile and kept for crystallization; after a few days red crystals were obtained suitable for X-ray analysis. Yield: 40%; mp >200 °C; Anal. Calcd. for $C_{34}H_{32}N_4O_{16}S_2U_2$: C, 31.59; H, 2.49; N, 4.33; Found: C, 31.46; H, 2.41; N, 4.29; IR (KBr pellet): $\nu$ (in $cm^{-1}$) 3434, 3061, 2927, 2362, 1659, 1555, 1482, 1375, 1318, 1251, 1190, 1045, 927, 881, 798, 744, 682, 604, 563, 492.

**Synthesis of $UO_2$(VI) Complex (4).** A solution of $UO_2(OAc)_2 \cdot 2H_2O$ (1.2 mmol) in acetonitrile (2 mL) was added to a solution of **L** (1.0 mmol) in acetonitrile (8 mL), and a similar procedure as described above was adopted. The precipitate was dissolved in acetonitrile, filtered, and kept for crystallization. After few days, yellow crystals formed which were suitable for X-ray analysis. Yield: 37%; mp >200 °C; Anal. Calcd. for $C_{38}H_{40}N_2O_{14}S_2U_2$: C, 35.41; H, 3.13; N, 2.17; Found: C, 35.34; H, 3.06; N, 2.10; IR (KBr pellet): $\nu$ (in $cm^{-1}$) 3430, 3057, 2925, 2865, 2362, 1658, 1553, 1484, 1374, 1251, 1190, 1048, 924, 819, 795, 743, 680, 602, 499, 426.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b03622.

Experimental details and spectroscopic data (PDF)

### Accession Codes

CCDC 1889546–1889548 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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