Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Bis(hydroxylamino)triazines: High Selectivity and Hydrolytic Stability of Hydroxylamine-Based Ligands for Uranyl Compared to Vanadium(V) and Iron(III)

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S Supporting Information



ABSTRACT: The development of ligands with high selectivity and affinity for uranium is critical in the extraction of uranium from human body, radioactive waste, and seawater. A scientific challenge is the improvement of the selectivity of chelators for uranium over other heavy metals, including iron and vanadium. Flat ligands with hard donor atoms that satisfy the geometric and electronic requirements of the U^{VI}O₂²⁺ exhibit high selectivity for the uranyl moiety. The bis(hydroxylamino)(triazine) ligand, 2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazine (H2bihyat), a strong binder for hard metal ions (Fe^{III}, Ti^{IV}, V^V, and Mo^{VI}), reacted with $[U^{VI}O_2(NO_3)_2(H_2O)_2] \cdot 4H_2O$ in aqueous solution and resulted in the isolation of the complexes $[U^{VI}O_2(bihyat)(H_2O)], [U^{VI}O_2(bihyat)_2]^{2-}, and {[U^{VI}O_2(bihyat)(\mu-OH)]}_2^{2-}.$ These three species are in equilibrium in aqueous solution, and their abundance varies with the concentration of H2bihyat and the pH. Reaction of H2bihyat with $[U^{VI}O_{2}(NO_{3})_{2}(H_{2}O)_{2}]$ 4H₂O in CH₃CN gave the trinuclear complex $[U^{VI}_{3}O_{6}(bihyat)_{2}(\mu-bihyat)_{2}]^{2-}$, which is the major species in organic solvents. The dynamics between the $U^{VI}O_2^{2+}$ and the free ligand H₂bihyat in aqueous and dimethyl sulfoxide solutions; the metal binding ability of the H₂bihyat over pyridine-2,6-dicarboxylic acid (H₂dipic) or glutarimidedioxime for U^{VI}O₂²⁺, and the selectivity of the H₂bihyat to bind U^{VI}O₂²⁺ in comparison to V^VO₄³⁻ and Fe^{III} in either U^{VI}O₂²⁺/V^VO₄³⁻ or U^{VI}O₂²⁺/Fe^{III} solutions were examined by NMR and UV–vis spectroscopies. The results revealed that H₂bihyat is a superior ligand for U^{VI}O₂²⁺ with high selectivity compared to Fe^{III} and V^VO₄³⁻, which increases at higher pHs. Thus, this type of ligand might find applications in the extraction of uranium from the sea and its removal from the environment and the human body.

INTRODUCTION

Over the past few years, an intense scientific effort has taken place to develop specific chelators for metal ions, including actinides, to combat environmental contamination caused by heavy metals, which is considered a serious and widespread health problem due to their high toxicity.^{1–5} Uranium has been the primary target for separation from the radioactive waste produced by nuclear industries and chelation therapy to be removed from human body.⁶ In the last few decades, multidentate complexing agents with oxygen donor atoms, based on phosphonic ligands $^{7-9}$ or siderophore-based units^{10,11} and polysulfides,¹²⁻¹⁶ have been identified as effective uranium chelators. Several of these ligands reduce $U^{VI}O_2^{2+}$ in both kidneys and skeleton¹⁷⁻²⁰ and have been

used successfully for separation of uranyl from mixed wastes and chemicals.^{21–24}

In addition, uranium is the principal fuel used in nuclear energy generation. However, because of the limited amounts of uranium in ground deposits, new technology is being developed for the extraction of uranyl from the sludge of the desalination plants due to its high abundance in the sea.^{25–28} This oceanic reserve would supply sufficient quantities of uranium for sustained zeroemission power production over 1000 years, if successfully harvested.

Received: March 6, 2018



At present, amidoxime-based adsorbents are considered to be the most promising materials for extraction of uranium from seawater.^{30–38} However, amidoximes, such as glutarimidedioxime (Scheme 1), lack selectivity for uranyl binding in the

Scheme 1



presence of high concentrations of transition metals, especially iron and vanadium,^{36,39} which strongly compete with uranium in the sequestration process.^{39–41} Several structural as well as speciation studies have been employed to better understand the ligand–uranyl binding process and design of strong selective ligands and polymer sorbents for uranium.^{36,37,42–45}

Currently, the design of sorbents for selectivity is dictated by the soft-hard acid-base properties of the metal ions and their geometric preferences. For example, the available coordination sites of $U^{VI}O_2^{2+}$ are in the equatorial plane, and thus, planar ligands with hard donor atoms that fulfill the ligation requirements of the $U^{VI}O_2^{2+}$ bind selectively the $U^{VI}O_2^{2+}$ moiety. The binding occurs through the equatorial pentacoordination or hexacoordination generally resulting in five- and six-membered chelate rings with multidentate ligands (Scheme 1).^{10,11,44-47}

A new family of compact nontoxic tridentate chelators, based on an N,N'-disubstituted bis(hydroxyamino)-1,3,5-triazine (BHT) motif, were reported to form hydrolytically stable complexes with hard acids, such as Fe^{III} and Ti^{IV}.^{48–50} Moreover, our group reported that these ligands also possess high affinity and hydrolytic stability for V^V and Mo^{VI} over a wide pH range of 3-11.^{51–53} The large thermodynamic stability of BHT ligands

Scheme 2. Synthetic Routes for the Complexes 1-4

with hard acids is due to the coordination of the metal ions to the two hard deprotonated hydroxylamine oxygens and a negatively charged heterocyclic nitrogen donor atoms. In addition, BHT ligands are planar, and thus, one or two ligands fit perfectly in the equatorial plane of $U^{VI}O_2^{2+}$. Apparently, the strong ligation of BHT ligands to the equatorial plane of $U^{VI}O_2^{2+}$ makes them strong candidates for the selective binding of uranyl in comparison to other hard metal ions.

Herein, we report the syntheses and structural and solution characterizations of four novel uranyl complexes coordinated with the ligand 2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazine (H₂bihyat; Scheme 1). To the best of our knowledge, the ligand H₂bihyat exhibits the strongest and most selective binding of $U^{VI}O_2^{2+}$ moiety in either $U^{VI}O_2^{2+}/Fe^{III}$ or $U^{VI}O_2^{2+}/V^VO_4^{3-}$ solutions at alkaline pHs.

EXPERIMENTAL SECTION

Caution! Uranium (primary isotope ²³⁸U) is a weak α -emitter (4.197 MeV) with a half-life of 4.47 × 109 years. All complexes were synthesized in monitored fume hoods, in a laboratory equipped with α - and β -counting equipment.

Materials and Methods. All chemicals and solvents were purchased from Merck. Microanalyses for C, H, and N were performed using a Euro-Vector EA3000 CHN elemental analyzer. Fourier transform infrared (FT-IR) transmission spectra of the compounds, in KBr pellets, were acquired using a JASCO-460 model spectrophotometer. The kinetic UV–vis measurements were recorded on a Photonics UV–vis spectrophotometer model 400, equipped with a CCD array, operating in the range from 250 to 1000 nm. The ligand H₂bihyat was synthesized with a modified procedure of the synthesis reported in ref 48 and is described in the Supporting Information. The ligand glutarimidedioxime was synthesized according to the procedure in ref 54, and the product was recrystallized from ethanol.

Synthesis of *trans*-[U^{VI}O₂(bihyat)(H₂O)₂]·H₂O (1). To a stirred aqueous solution (20 mL) of H₂bihyat (13 mg, 0.051 mmol) was added one portion (26 mg, 0.051 mmol) of $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O (pH \approx 4). Upon addition of the uranyl salt, the reaction mixture became brown, indicating complex formation. Brown crystals deposited upon the partial slow evaporation of the mother liquor. The crystalline solid



	1	2	3	4	ł
U(1)-O(1)	1.788(3)	1.805(6)	1.785(4)	1.796(5)	1.798(5)
U(1) - O(2)	1.774 (3)	1.809(6)	1.790(5)	1.786(6)	
U(1) - O(4)	2.359(3)	2.415(4)	2.354(5)	2.315(5)	2.461(6)
U(1) - O(3)	2.412(3)	2.447(4)	2.376(4)	2.405(6)	2.450(5)
U(1) - N(3)	2.436(4)	2.518(5)	2.418(5)	2.440(7)	2.502(7)
$U(1) - O(7)^{b}$	2.367(4)				
$U(1) - O(6)^{b}$	2.380(3)		2.354(4)		
$U(2) - O(3')^{c}$				2.391(5)	
$U(2)-N(1')^{c}$				2.880(6)	
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^{*a*}The two columns under 4 are referred to U(1) and U(2) atoms, respectively. ^{*b*}Terminal H₂O molecules for 1, μ -OH for 2. ^{*c*}Bonds of U(1) atoms with side-on $-N(CH_3)O$ coordination.

Table 2. Selected Bond Angles	s (deg) for	Compounds	1-4
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	1	2	3	2	ŀ
O(2) - U(1) - O(1)	175.5(1)	177.6(3)	178.0(2)	177.4(3)	
O(2) - U(1) - N(3)	91.1(1)	88.1(1)	95.9(2)	83.6(2)	97.0(2)
O(1) - U(1) - N(3)	93.0(1)	91.8(1)	86.2(2)	96.7(2)	83.0(2)
O(4) - U(1) - N(3)	63.5(1)	61.1(1)	63.6(2)	64.3(2)	61.5(2)
O(3) - U(1) - N(3)	63.3(1)	60.7(1)	63.2(2)	62.4(2)	60.8(2)
$O(4) - U(1) - O(6)^{b}$	74.8(1)		84.5(1)		
$O(7) - U(1) - O(6)^{b}$	86.0(1)		74.0(1)		
$O(7) - U(1) - O(3)^{b}$	72.4(1)		75.3(1)		
$O(x)-U(1)-O(y)^{c}$		58.9(1)		60.4(2)	59.7(2)
O(3) - U(2) - O(4')				75.0(2)	
O(3')-U(2)-N(1')				29.5(2)	
O(4) - U(2) - O(3')				98.9(2)	

^aThe two columns under 4 are referred to as U(1) and U(2) atoms, respectively. ^bAngles between terminal H₂O molecules for 1, μ -OH for 2. ^cAngles between neighboring bihyat²⁻ ligands.

was recovered by filtration, washed with a minimum amount of cold water, and dried under vacuum. Yield: 15 mg (51%, based on H₂bihyat). IR (ATR, cm⁻¹): 1531 [ν (-C=N-), s] 904 [ν _{as}(U=O), s], 855 [ν _s(U=O), w]. Anal. Calcd for C₉H₂₀N₆O₈U (M_r = 578.3): C, 18.69; H, 3.49; N, 14.53; Anal. Found C, 18.69; H, 3.41; N, 14.54%.

Synthesis of *trans*-Na₂[U^{Vi}O₂(bihyat)₂]-2H₂O (2). To a stirred aqueous solution (2 mL) of H₂bihyat (20 mg, 0.078 mmol) was added one portion (20 mg, 0.039 mmol) of $[U^{Vi}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O. The reaction mixture became brown, and the pH was adjusted to 11 with ca. 130 µL of a 10% w/v NaOH solution. The solution was layered with methyl alcohol, and brown crystals of compound 2 suitable for X-ray diffraction analysis were formed after 5 d. The crystalline solid was recovered by filtration, washed with a minimum amount of methyl alcohol, and dried under vacuum. Yield: 15 mg (45%) based on H₂bihyat. IR (ATR, cm⁻¹): 1535 [ν (-C=N-), s] 846 [ν _{as}(U=O), s], 761 [ν _s(U=O), w]. Anal. Calcd for C₁₈H₃₂Na₂N₁₂O₁₀U (M_r = 860.6): C, 25.12; H,3.75; N, 19.53; Anal. Found C, 25.16; H, 3.69; N, 19.48%.

Synthesis of K₂[U^{VI}₂O₄(\mu_2-OH)₂(bihyat)₂]·3H₂O (3). To a stirred aqueous solution (4 mL) of H₂bihyat (20 mg, 0.078 mmol) was added one portion (39 mg, 0.078 mmol) of [U^{VI}O₂(NO₃)₂(H₂O)₂]·4H₂O. The reaction mixture became brown, and the pH was adjusted to 9 with ca. 175 \muL of a 10% w/v KOH solution. The solution was layered with methyl alcohol, and brown crystals of compound 3 suitable for X-ray diffraction analysis were formed after 8 d. The crystalline solid was recovered by filtration, washed with a minimum amount of methyl alcohol, and dried under vacuum. Yield: 18 mg (38%) based on H₂bihyat. IR (ATR, cm⁻¹): 1554 [\nu(-C=N-), s] 887 [\nu_{as}(U=O), s], 825 [\nu_s(U=O), w]. Anal. Calcd for C₁₈H₃₆K₂N₁₂O₁₅U₂ (M_r = 1214.58): C, 17.78; H, 2.98; N, 13.83; Anal. Found C, 17.70; H, 2.93; N, 13.89%.

Synthesis of $(\text{Et}_3\text{N})_2[\text{U}^{VI}_3\text{O}_6(\text{bihyat})_4]$ ·4CH₃CN (4). Sequential addition of $[\text{U}^{VI}\text{O}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ ·4H₂O (26 mg, 0.052 mmol) and triethylamine (14 mg, 0.138 mmol,19 μ L) into a stirred hot (70 °C) acetonitrile (2 mL) solution of H₂bihyat (18 mg, 0.069 mmol) resulted

in a clear brown solution. The solution was left undisturbed at ambient temperature (25 °C) for 2 d, and brown crystals suitable for X-ray diffraction analysis were obtained. The crystals were recovered by filtration and dried under vacuum. Yield: 32 mg (85%) based on H₂bihyat. IR (ATR, cm⁻¹):1535 [ν (-C=N-), s] 902 [ν _{as}(U=O), s], 855 [ν _s(U=O), w]. Anal. Calcd for C₅₆H₁₀₀N₃₀O₁₈U₃ (M_r = 2195.7): C, 30.63; H, 4.59; N, 19.14; Anal. Found C, 30.56; H, 4.60; N, 19.18%.

RESULTS AND DISCUSSION

Synthesis of the Compounds 1–4. The uranyl complexes 1–4 were synthesized according to Scheme 2. The complexes 1–3 were obtained in a one-pot reaction, in which $[U^{VI}O_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ reacted with H_2 bihyat in aqueous solution at a molar ratio of $U^{VI}O_2^{2+}/H_2$ bihyat 1:1 for 1 and 3 (eq 1) and 1:2 for 2.

$$2[U^{VI}O_{2}(NO_{3})_{2}(H_{2}O)_{2}]\cdot 4H_{2}O + 2H_{2}bihyat + 6KOH$$

$$\rightarrow K_{2}[(U^{VI}O_{2})_{2}(\mu - OH)_{2}(bihyat)_{2}] + 4KNO_{3} + 12H_{2}O$$
(1)

The synthesis of the trinuclear compound **4** was accomplished by reacting $[U^{VI}O_2(NO_3)_2(H_2O)_2] \cdot 4H_2O$ with the ligand H_2 bihyat in CH₃CN at a molar ratio of $U^{VI}O_2^{2+}/H_2$ bihyat 3:4 in the presence of Et₃N (8 equiv) to deprotonate the ligand (eq 2).

$$3[U^{VI}O_{2}(NO_{3})_{2}(H_{2}O)_{2}] \cdot 4H_{2}O + 4H_{2}bihyat + 8Et_{3}N$$

$$\rightarrow (Et_{3}NH)_{2}[(U^{VI}O_{2})_{3}(\mu-bihyat)_{2}(bihyat)_{2}]$$

$$+ 6Et_{3}NHNO_{2} + 18H_{2}O$$
(2)

The mononuclear complex 1 is slightly soluble in water at pH = 7 and above. Compounds 1–4 are insoluble in CH₃CN but very soluble in dimethyl sulfoxide (DMSO) and H₂O at pH \geq 6. At pH < 6 all U^{VI}O₂²⁺ precipitates out as 1 and is insoluble. Thus, all solution studies were performed at pH values above 6.0.

At this point, it is worth noting that the uranyl complexes 1, 2, and 4 in DMSO and 1, 2, and 3 in H_2O solution at $pH \ge 6$ are in a dynamic equilibrium, as it was found by NMR spectroscopy (vide infra).

X-ray Crystallographic Results. A summary of the crystallographic data and the final refinement details for compounds 1–4 are given in Table S1. Interatomic distances and bond angles relevant to the uranium coordination sphere are listed in Tables 1 and 2.

The crystal structure of 1 is shown in Figure 1A. The uranium(VI) atom adopts the classical pentagonal bipyramidal



Figure 1. ORTEP diagram of the mononuclear complexes **1** (A) and **2** (B) with 50% probability ellipsoids (hydrogen atoms and solvent molecules were omitted for clarity).

configuration and is bonded to a tridentate bihyat²⁻ ligand through the pyridine-like nitrogen atom N(3), $[d(U-N_{tr}) =$ 2.436(4) Å] and the two deprotonated hydroxylamine hydroxyls O(3), O(4) $[d_{mean}(U-O_h)= 2.374(4) \text{ Å}]$ as well as two oxygen atoms O(6) and O(7) $[d_{mean}(U-O_w)= 2.386 \text{ Å}]$ of two water molecules and two trans oxido groups O(1) and O(2), $[d_{\text{mean}}(U=O) = 1.781(3) \text{ Å}]^{.55,56}$ The equatorial plane defined by the U, O(3), N(3),O(4), O(6), and O(7) atoms [root-meansquare (rms) deviation 0.060 Å] is perpendicular to the linear *trans*- $[U^{VI}O_2]^{2+}$ moiety $[(O=U=O)^{-} = 175.5(1)^{\circ}]$. At this point, it is worth noting that the $U^{VI}-N_{tr}$ bond distance of 2.436(4) Å is indicative of a very strong bond of the pyridine-like triazine nitrogen to uranium(VI). The dipicolinate analogue of 1, trans- $[U^{VI}O_2(\text{dipic})(H_2O)_2]$ (H₂dipic = pyridine-2,6-dicarbox-ylic acid), has a $U^{VI}-N_{py}$ bond length of 2.520(6) Å,⁴⁷ and in general, the $U^{VI}O_2^{2+}$ complexes with tridentate ligands containing pyridine nitrogens ligated to uranium(VI) have U^{VI} – N_{pv} bond length in the range of 2.52–2.64 Å.^{46,47,57–60} The ligand bihyat²⁻ exhibits two resonance structures **A** and **B** (Scheme 3).^{52,53} The flat sp² hybridized hydroxylamine nitrogen atoms are in agreement with a large contribution of the structure "B". The structure B presented in Scheme 3, according to which all out-of-ring nitrogen atoms are of approximately sp² configuration, and thus, the inner ring nitrogen atoms, including the one ligated to uranium, possess high electron densities.



Therefore, a strong electron donation from the ring nitrogen atom to uranium takes place, and this results in a very strong $U^{VI}-N$ bond. The same trend for the $U^{VI}-N_{tr}$ bond distances is observed in the structures of compounds 2, 3, and 4 (see Table 1).

The anion of the mononuclear complex 2 (Figure 1B) has a hexagonal bipyramidal structure with the six donor atoms of two tridentate bihyat²⁻ ligands and the uranium(VI) atom [rms deviation 0.082 Å] to occupy the equatorial plane, which is perpendicular to the linear trans- $[U^{VI}O_2]^{2+}$ moiety [(O=U=O) = $177.6(3)^{\circ}$]. Uranyl oxido bond lengths for the eightcoordinated ion of 2 $[d_{\text{mean}}(U=O) = 1.807(6) \text{ Å}]^{54,61,62}$ are slightly longer than those in the seven-coordinate complex 1 $[d_{\text{mean}}(U=O) = 1.781(3) \text{ Å}]$ and the U^{VI}-N_{tr} [2.518(5) Å] and $U-O_h$ [mean value = 2.431(4) Å] bonds are also longer for the anion of 2 cf. 2.436(4) and 2.386(3) Å for 1. This bond lengthening in the anion of 2 might be attributed to the higher coordination number (eight) of it in comparison to seven for 1. However, in two compounds $[U^{VI}O_2(dipic)(H_2O)_2]$ and $[U^{VI}O_2(dipic)_2]^{2-}$, which are the analogues of 1 and the anion of 2, respectively, the uranyl oxido bond lengths are almost identical $[\sim 1.77 \text{ Å}]$,^{46,47} and thus, the lengthening of U^{VI}=O bonds in the anion of 2 in comparison to 1 was attributed to the strong binding of the two bihyat²⁻ ligands to the equatorial plane of the anion of 2. The longer U=O bond lengths for 2 in relation to 1, 3, and 4 (see Table 1) are nicely reflected in the ν_{as} (U=O), which is 846 cm⁻¹ for 1 and ~900 cm⁻¹ for 1, 3, and 4 (vide supra).

The structure of the anion of 3 (Figure 2) consists of two distorted pentagonal bipyramidal uranyl units each bridged by



Figure 2. ORTEP diagram of dinuclear complex 3 with 50% probability ellipsoids (hydrogen atoms and solvent molecules were omitted for clarity).

two hydroxido groups in a centrosymmetric dimer. Each uranyl group is bonded to a tridentate bihyat^{2–} ligand through two hydroxylamino oxygen donor atoms and the central triazine nitrogen atom. The structural features of the anion of **3** are very similar to those of **1**.

The structure of the anion of 4 (Figure 3) consists of three distorted hexagonal bipyramidal uranyl units bridged by two bihyat^{2–} ligands in a centrosymmetric trimer [U(1) is the center



Figure 3. ORTEP diagram of the trinuclear anion of 4 with 50% probability ellipsoids (hydrogen atoms and solvent molecules were omitted for clarity).

of symmetry]. The uranyl group $U(2)O_2^{2+}$ and its symmetry related $U(2A)O_2^{2+}$ are bonded to a tridentate bihyat²⁻ ligand through two deprotonated hydroxylamine hydroxyls and the central triazine nitrogen atom and are bridged with $U(1)O_2^{2+}$ group with two bihyat²⁻ligands. One hydroxylamino group of the bridging bihyat²⁻ bridges the two uranyl groups through its oxygen atom, while the other hydroxylamino group of the same ligand bridges the two uranyl groups in a side-on fashion. This mode of bridging action of bihyat²⁻ is the first example to be reported. The N atom of the hydroxylamines in all complexes is sp² hybridized, and thus, it has a flat trigonal geometry. However, the N atom of the hydroxylamine ligated to the uranium atom with a side-on mode has a trigonal pyramidal geometry, and thus, in 4, are sp³ hybridized, as expected, so that the unpaired electrons of the N atom are available for donation to U^{VI} ion.

The three uranium(VI) atoms are arranged in a linear fashion $[U(2A)-U(1)-U(2) = 180^{\circ}]$.

Speciation, Dynamic, and Stability-Selectivity Studies of Complexes 1–4 by NMR Spectroscopy. Complexes 1–4 were characterized by ¹H NMR spectroscopy in DMSO- d_6 and D₂O solutions. However, irrespective of the uranyl complex 1–4 dissolved in either DMSO- d_6 or D₂O the uranyl complexes 1, 2, 4 and 1–3 were formed in DMSO- d_6 and D₂O, respectively, and their concentration was dependent on the initial concentration of the uranyl complexes and the pHs of the aqueous solutions. The ¹H NMR signals of the uranyl complexes were broad and overlapping, and thus, two-dimensional (2D) {¹H, ¹³C} HMQC NMR (Figures S1 and S2) spectroscopy was used to resolve and assign the signals. The ¹H and ¹³C chemical shifts of the uranyl complexes 1–4 are reported in Table 3.

The broad peaks reveal the existence of dynamic processes between the $U^{VI}O_2^{2+}$ -bihyat²⁻ species and between the uranyl species and the free ligand. To study this dynamic behavior 2D

{¹H} EXSY NMR spectra were acquired in both organic and aqueous solutions.

In addition, the hydrolytic stability of $U^{VI}O_2^{2+}$ -bihyat²⁻ complexes was studied in the presence of the competing for $U^{VI}O_2^{2+}$ ligand dipicolinic acid (H₂dipic). Moreover, the selectivity of bihyat²⁻ to bind $U^{VI}O_2^{2+}$ in $U^{VI}O_2^{2+}/V^VO_4^{3-}$ and $U^{VI}O_2^{2+}/Fe^{III}$ solutions was also investigated with ¹H NMR spectroscopy. The drawings of all species that are formed in these experiments were depicted in Scheme 4.

NMR in Organic Solvents. The ¹H NMR spectrum of the free ligand H_2 bihyat in DMSO- d_6 solution gave peaks at 3.28, 3.63, and 3.74, which were assigned to the methyl hydroxylamino (H_f) , -N(CH₂)- morpholino, and -(CH₂)- morpholino protons, respectively (Scheme 2).

In the solution $(CD_3CN/DMSO-d_6)$ the species 2, 4, and 5 are formed, as it is evident by ¹H NMR spectroscopy (Scheme 4). In particular, the uranyl complex 4, in a mixed-solvent system of $CD_3CN/DMSO-d_6$ (4:1), gave peaks in ¹H and 2D {¹H, ¹³C} HMQC NMR spectra, which were assigned to complex 4 (96%), to the mononuclear complex $[(U^{VI}O_2)(bihyat)_2(DMSO-d_6)_2]$ (5) (3%) and to the free H₂bihyat (1%) (Figure S1). The NMR spectra show for complex 4 two different chemical shifts for the hydroxylamine methyl protons and carbons at 3.636 (38.21) and 3.598 (37.50) ppm, which were assigned to the hydroxylamines with sp³ (H_a) and sp² (H_{c,b}) hybridized N atom, respectively (in parentheses the chemical shifts of ¹³C nuclei). A solution of compound 4 in DMSO-d₆ gave ¹H NMR peaks from 4, 5, and free H₂bihyat. Free H₂bihyat is produced from 4 according to eq 3.

$$[U^{VI}_{3}O_{6}(bihyat) +_{4}]^{2^{-}} + 2H^{+} + 6DMSO - d_{6}$$

$$\rightarrow 3[(U^{VI}O_{2})(bihyat)_{2}(DMSO - d_{6})_{2}] + H_{2}bihyat \qquad (3)$$

The ¹H NMR spectra of DMSO- d_6 solutions containing H₂bihyat (5-30 mM) and $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O (10 mM) gave peaks assigned to the complexes 3, 4, and 5 (Figure 4A). The hydroxylamino methyl protons for each of the species 3 (H_g) , 4 (H_b, H_c) , and 5 (H_e) , gave a peak at 3.60 ppm. The ¹H NMR triplets of morpholino methylene protons of the three complexes are overlapping at 3.67 and 3.80 ppm. Moreover, complex 4 gave a peak at 3.64 ppm, which was assigned to the hydroxylamino methyl protons attached to the two sp³ hydroxylamine N atoms. Addition of H₂bihyat (10.0 mM) to a DMSO- d_6 solution of $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O(10.0 mM) mainly leads to the formation of 5(90%) and of a minor quantity of 4 (10%) (Figure 4A). The concentration of the trinuclear complex 4 increases at higher concentrations (up to 17.5 mM) of H₂bihyat, whereas the quantity of 5 decreases. At H₂bihyat concentrations greater than 17.5 mM the quantity of complex 4 decreases, whereas the integral of the peak at 3.60 ppm increases (Figure 4). The increment of the intensity of the peak at 3.60

Table 3.	$^{1}H(^{13}C)$	Chemical	Shifts (ppm) of Com	plexes 1-4	and H ₂ bihyat ^a

compounds	$H_a(C_a)$	$H_{b-f}(C_{b-f})$	$-N(CH_2)_2 - (CH_2)_2O$	$-N(CH_2)_2 - (CH_2)_2O$
H ₂ bihyat (DMSO- <i>d</i> ₆)		3.276(37.51)	3.627(66.48)	3.736(43.81)
$1 (D_2 O pH = 9.5)$		3.651(37.85)	3.680(66.55)	3.722(43.99)
$1 (DMSO-d_6)$		3.598(37.50)	3.670(66.57)	3.800(44.13)
2 (D ₂ O pH = 9.5)		3.604(37.60)	3.746(66.49)	3.748(43.93)
$3 (D_2 O pH = 9.5)$		3.731(37.79)	3.766(66.55)	3.816(43.99)
4 (DMSO- d_6)	3.636(38.21)	3.598(37.50)	3.670(66.57)	3.800(44.13)

^aNMR (¹³C) shifts from 2D {¹H, ¹³C} grHMQC. Labeling according to Scheme 2.

Scheme 4. Drawings of the U^{VI}, V^V, and Fe^{III} Species Formed with H₂bihyat and H₂dipic



Figure 4. ¹H NMR spectra, assignments of the peaks (A) and speciation (based on the ¹H NMR spectra) of the uranyl complexes (B) of DMSO- d_6 solutions containing $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O (10.0 mM) and H₂bihyat (5.00–25.0 mM). **5** and $[U^{VI}O_2(bihyat)_2]^{2-}$ (\blacksquare), $[(U^{VI}O_2)_3(bihyat)_3]^{2-}$ (\blacklozenge), H₂bihyat (red triangles), $U^{VI}O_2^{2+}$ (\blacklozenge). Labeling according to Scheme 2.

ppm was assigned to the formation of complex 2. However, the quantity of 2 was not measured because of the overlap of the peaks of 2 with those of 5.

NMR in Aqueous Solution. The ¹H NMR spectrum of the ligand H_2 byhyat in D_2O at pD 9.5 gave a peak at 3.25 and a multiplet at 3.70 ppm, which were assigned to the methyl hydroxylamino (H_f) and the -N(CH₂)-(CH₂)O- morpholino protons, respectively.

In D₂O solutions of $U^{VI}O_2^{2+}$ and H₂bihyat the species **1**, **2**, and **3** are formed, as it is evident by ¹H NMR spectroscopy (Scheme 4). The ¹H NMR spectra of the complexes **1**–4 in D₂O at pDs > 5 gave peaks that were assigned to complex **1** and anions of

complexes 2 and 3. The ¹H NMR spectra of the D₂O solutions containing $[U^{VI}O_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (5.00 and 10.0 mM) and H₂bihyat (2.00–30.0 mM) at various pDs gave also peaks assigned to the proton complex 1 and anions of complexes 2 and 3, being in dynamic equilibria (Figure 5). 1 and the anion of 3 are more stable at 1:1 $U^{VI}O_2^{2+}/H_2$ bihyat molar ratio, whereas addition of more H₂bihyat results in the formation of the anion of 2, which is the only species present in the solution at 1:2 $U^{VI}O_2^{2+}/H_2$ bihyat molar ratio. The stability of 2 increases over 1 and 3 at higher pDs. At 1:2 $U^{VI}O_2^{2+}/H_2$ bihyat molar ratio no observed peaks originated from the free ligand, and this fact reveals that H₂bihyat forms hydrolytically stable complexes with



Figure 5. ¹H NMR spectra of the D₂O solutions, at various pDs, containing 10.0 mM $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O and H₂bihyat (9.50 mM) (solid black line), 10.0 mM $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O and H₂bihyat (18.0 mM) (red dashed line), and 5.00 mM $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O and H₂bihyat (4.75 mM) (solid green line). Labeling according to Scheme 2.

 $U^{VI}O_2^{2+}$. More specifically, solutions containing $[U^{VI}O_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ and H_2 bihyat at a molar ratio $\sim 1:1 (10.0/9.50 \text{ mM})$ show the formation of complex 1, the anion of 3, and minor quantities of the anion of 2 in the pD range of 4–12. The ¹H NMR spectrum of complex 1 in D₂O gave broad peaks at 3.65, 3.68, and 3.72, which were assigned to the H_e , $-N(CH_2)$ -, and $-(CH_2)O$ - morpholino protons, respectively. Complex 1 is more stable at pDs < 5, where it precipitates out due to its limited solubility in D₂O. At pDs > 5 the anion of 3 is the dominant species in solution giving in ¹H NMR spectra a sharp peak, relative to the peaks of the other $U^{VI}O_2^{2+}$ /bihyat^{2–}species, at 3.731 ppm, which was assigned to methyl hydroxylamino

protons (H_d) and two discrete triplets at 3.766 and 3.816 ppm, which were assigned to $-N(CH_2)$ - and $-(CH_2)O$ - morpholino protons, respectively. Small quantities of the anion of **2** are formed at high pDs, pD \approx 9.

 D_2O solutions containing $[U^{VI}O_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ and H_2 bihyat in a molar ratio of ~1:2 (10.0/18.0 mM) show mainly the formation of the anion of **2**, whereas **1** and the anion of **3** are present in minor quantities. The quantity of the anion of **2** in this solution increases by increasing the pD value. At pDs 7.3, and 9.0, 80% and 95% of H_2 bihyat is bound to the anion of **2**, respectively. The ¹H NMR spectrum of complex **2** in D_2O shows a peak at 3.60 ppm, which was assigned to methyl hydroxylamino protons (H_g) and only one peak for the morpholino protons at 3.75 ppm.

Ďynamic NMR in Organic Solvents. The 2D $\{^{1}H\}$ EXSY NMR of 4 in DMSO- d_6 /CD₃CN (1:4, v/v) shows off-diagonal exchange cross peaks, starting from the strongest to the weakest, between H_a and H_b , H_a and H_f and H_c and H_f (Figure S3), which were assigned to three different exchange pathways (Scheme 5, pathways 1–3). The $H_a - H_b$ exchange is attributed to the change of the hybridization, from sp³ to sp² and the reverse, of the two nonequivalent hydroxylamine nitrogen atoms located on each of the two bihyat2- ligands ligated to the central uranyl moiety (pathway 1, Scheme 5). The $H_a - H_f$ is attributed to the exchange of the central bihyat^{2–} ligands with the free H_2 bihyat (pathway 2, Scheme 5). However, the fact that H_b does not exchange with the free ligand as fast as H_a does supports a stepwise mechanism, whereas the chelate rings of the central $bihyat^{2-}$ initially open at Nsp^3 hydroxylamine; then, the coordinated N_{sp2} turns to N_{sp3} , and finally H_2 bihyat dissociates. The lability of the $U^{VI}O_2^{3+}$ $O(N_{sp3})$ bond compared to that of $U^{VI}O_2^{2+}$ - $O(N_{sp2})$ might be attributed to the more efficient protonation of $O(N_{sp3})$ compared to $O(N_{sp2})$. However, if someone considers that all metal complexes with bihyat²⁻, including the rest of the uranium complexes in this study, coordinate to N_{sp2} hydroxylamines, the

Scheme 5. Exchange Mechanisms of Complex 4 in DMSO- d_6 /CD₃CN 1:4 (v/v)



 N_{sp3} hydroxylamine in 4 must exhibit higher energy than N_{sp2} , which is stabilized by the side-on coordination with the second uranium atom, and thus, it is more labile. The much lower exchange rate of H_c-H_f was attributed to the exchange of the bihyat²⁻ in complex 5 with the free ligand (pathway 3, Scheme 5), supporting that $U^{VI}O_2^{2+}-O(N_{sp2})$ is more inert than $U^{VI}O_2^{2+}-O(N_{sp3})$.

Dynamic NMR in Aqueous Solutions. The 2D {¹H} EXSY NMR spectra of D₂O solutions containing $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O and H₂bihyat at pD 8.0 and 9.5 are shown in Figure S4. The spectra gave off-diagonal exchange cross peaks between the protons H_d-H_e and H_e-H_g. The H_d-H_e were assigned to the dimerization of 1 to 3 and the reverse (Scheme 6, pathway 1). The less-intense H_e-H_g cross peaks were

Scheme 6. Exchange Mechanisms of 1-3 in D_2O



assigned to the ligation–deligation of a bihyat^{2–} in the conversion of 1 to 2 and the reverse (Scheme 6, pathway 2). The exchange of the ligated bihyat^{2–} to $U^{VI}O_2^{2+}$ with the free H₂bihyat in D₂O is a slow process in agreement with the results in DMSO- d_6 /CD₃CN.

NMR Experiments with H_2 dipic and H_2 bihyat. In the D₂O solutions containing U^{VI}O₂²⁺, H₂bihyat, and H₂dipic the species 1, 2, 3, and 6 are formed, as it is evident by ¹H NMR

spectroscopy (Scheme 4). The ¹H NMR spectra of the D_2O solutions containing $[U^{VI}O_2(NO_3)_2(H_2O)_2] \cdot 4H_2O$ (5.00 mM), H₂bihyat (13.0 mM), and various concentrations of H₂dipic (0-20.0 mM) at pDs 7.5 and 9.0 are shown in Figure 6A. Each ¹H NMR spectrum contains peaks assigned to the free H₂bihyat and H_2 dipic, to the anion of complex 2, and to a new complex that contains both bihyat²⁻ and dipic²⁻ ligated to the uranyl moiety, that is, $[U^{VI}O_2(bihyat)(dipic)]^{2-}(6)$ (Figure 6A, Scheme 4). The ¹H NMR spectrum of complex 6 exhibits a multiplet at 8.44 assigned to the aromatic protons of the ligated dipic^{2–}, a triplet at 3.79 assigned to the $-(CH_2)O$ - morpholino protons of bihyat²⁻, a triplet at 3.75 assigned to the -N(CH₂)- morpholino protons of bihyat²⁻, and a singlet at 3.685 ppm assigned to the methylhydroxylamine protons of bihyat²⁻. The diagram of the concentrations of the anion of 2 and 6 versus the concentration of the added H₂dipic is shown in Figure 6B. The ¹H NMR spectrum of a D_2O solution containing $[U^{VI}O_2(NO_3)_2(H_2O)_2]$. 4H₂O (5.00 mM), H₂bihyat (13.0 mM), and H₂dipic (10.0 mM) reveals the presence of complex 6 (67%) and of the anion of 2(33%) at pD 7.5, while at pD 9 the ratio changes to 7% and 93% for 6 and the anion of 2, respectively. The equilibrium constants calculated for reaction 4 are 0.60 ± 0.05 and 52 ± 5 at pDs 7.5 and 9.0, respectively.

$$[U^{VI}O_{2}(bihyat)(dipic)]^{2^{-}} + H_{2}bihyat$$

$$\rightleftharpoons [U^{VI}O_{2}(bihyat)_{2}]^{2^{-}} + H_{2}dipic$$
(4)

The stability of complex 6 is related to the $U^{VI}O_2/bihyat^{2-}$ species that exists in D_2O at various pDs. At low pDs the 1:1 $U^{VI}O_2/bihyat^{2-}$ species, that is, $[U^{VI}O_2(bihyat)(H_2O)_2]$ (1'), is the most stable complex, and at the equatorial plane of 1' there is space for dipic²⁻ to bind to the uranium atom, while at high pDs the complex $[U^{VI}O_2(bihyat)_2]$ (2') is the most stable, and in 2' there is not any space for dipic²⁻ to ligate to the uranyl moiety. Thus, the speciation in D_2O of the system $[U^{VI}O_2(NO_3)_2(H_2O)_2] \cdot 4H_2O - H_2bihyat - H_2dipic is entirely$ $controlled by the ligation of bihyat²⁻ to <math>U^{VI}O_2^{2+}$.

Furthermore, despite the high affinity of H₂dipic for U^{VI}O₂²⁺ {the stability constants, $log(\beta_i)$, for the two complexes $[U^{VI}O_2(dipic)]$ and $[U^{VI}O_2(dipic)_2]^{2-}$ are 10.7 ± 0.1 and 16.3



Figure 6. ¹H NMR spectra (A) and speciation of the uranyl complexes on the basis of ¹H NMR spectra (B) of D₂O solutions containing $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ -4H₂O (5.00 mM) and H₂bihyat (13.0 mM) and various concentrations of H₂dipic (0–20.0 mM) at pD 7.5 (red lines) and pD 9 (black lines). Labeling according to Scheme 2.



Figure 7. Speciation and ¹H NMR spectra of the uranyl complexes of D_2O solutions containing $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4 H_2O (10.0 mM), H_2 bihyat (20.8 mM), and NaVO₃ (0–15.0 mM) at pDs 8.0 (A, C) and 10.0 (B, D).

 \pm 0.1 {Xu, 2013}, respectively} H₂dipic cannot displace bihyat²⁻ from U^{VI}O₂²⁺/bihyat²⁻ species. This means that the thermodynamic stability of U^{VI}O₂²⁺/bihyat²⁻ complexes is much higher than that of the corresponding U^{VI}O₂²⁺/dipic²⁻ complexes.

NMR Experiments with Glutarimidedioxime and H₂bihyat. The ¹H NMR spectra of the D₂O solutions containing $[U^{VI}O_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (5.00 mM), H₂bihyat (13.0 mM), and various concentrations of glutarimidedioxime (2.5–27.0 mM) at pDs 7.5 and 9.0 are shown in Figure S5. The spectra show that, in the presence of H₂bihyat, glutarimidedioxime does not form any complex with $U^{VI}O_2^{2+}$ even if the molar ratio of glutarimidedioxime/H₂bihyat is greater than or equal to 2. Thus, considering the high stability of $U^{VI}O_2^{2+}$ -glutarimidedioxime complex,^{41,54} these results support the high affinity of H₂bihyat for the uranyl moiety.

H₂bihyat Binding of U^{VI}O₂²⁺ in U^{VI}O₂²⁺/V^VO₄³⁻ Solutions by ¹H NMR Spectroscopy. In D₂O solutions containing U^{VI}O₂²⁺, H₂bihyat, and V^VO₄³⁻ the species 1, 2, 3, 7, and $[V^{V}O_{2}(bihyat)]^{-}$ are formed, as it evident by ¹H NMR spectroscopy (Scheme 4). The ¹H NMR spectra of D₂O solutions containing $[U^{VI}O_{2}(NO_{3})_{2}(H_{2}O)_{2}]\cdot 4H_{2}O$ (10 mM), H₂bihyat (20.8 mM), and various quantities of NaV^VO₃ (0–15.0 mM) at pDs 8.0 and 10.0 are shown in Figure 7C,D. The diagrams of the concentrations of the $U^{VI}O_{2}^{2+}/bihyat^{2-}$ and $V^{V}O_{3}^{+}/bihyat^{2-}$ species versus the concentration of the added NaV^VO₃ at pDs 8.0 and 10.0 are shown in Figure 7A,B. The ¹H NMR spectrum of D₂O solution containing $[U^{VI}O_{2}(NO_{3})_{2}(H_{2}O)_{2}]\cdot 4H_{2}O$ (10.0 mM) and H₂bihyat (20.8 mM) reveals the presence of the anion of **2** and the free ligand at

both pDs. The stepwise addition of NaV^VO₃ to the solution results in the decrease of the anion of 2 and the free ligand and the simultaneous formation of a new complex with peaks at 3.255 [-(CH₃)NOH], 3.664 [-N(CH₂)-], and 3.742 [-(CH₂)O-] ppm. Stability studies of the mixed inorganic UVIO22+/VVO43solutions have shown the formation of $(U^{VI}O_2)_3(V^VO_4)_2$ which is the dominant species at pH range of 1.5-9.5.63 The integration of the peaks in the ¹H and ⁵¹V spectra of the new $U^{VI}O_2^{2+}/V^VO_4^{3-}/H_2$ bihyat complex reveals that its stoichiometry is 3:2:2, that is, $[(U^{VI}O_2)_3(V^VO_4)_2(H_2bihyat)_2]$ (7). The chemical shifts of the peaks of the ligand of complex 7 are only slightly shifted to weaker field compared to the free ligand, and this indicates that the ligand is likely to be in the protonated form H₂bihyat. In addition, the peaks of the ligated H₂bihyat do not show any broadening, although they are very close to the peaks of free H₂bihyat. Apparently, the ligation of the H₂bihyat to the $(U^{VI}O_2)_3(V^VO_4)_2$ is inert. ⁵¹V NMR spectroscopy shows a broad peak at -514 ppm assigned to 7 (Figure S6).

Complex 7 is the major species (59%), in a solution containing 10.0 mM UO^{V1}₂(NO₃)₂, 20.8 mM H₂bihyat, and 10.0 mM NaV^VO₃, at pD = 8.0, while at pD = 10.0 the anion of **2** is the major species (50%), and 42% is complex 7. A small quantity of H₂bihyat, less than 5%, is bound to the complex *cis*-[V^VO₂(bihyat)]⁻. The concentration of *cis*-[V^VO₂(bihyat)]⁻ decreases when the concentration of NaV^VO₃ is increased to 15 mM with a simultaneous increase of 7. In any case, the data show that bihyat²⁻ ligates to U^{VI}O₂⁺ much more strongly than to V^VO₂⁺, despite the high stability of the VO₂⁺-bihyat²⁻ complexes (the stability constants [log(β_i)] for [HV^VO₂(bihyat)] and *cis*-



Figure 8. ¹H NMR spectra of a D₂O solution containing H₂bihyat (10.5 mM) and $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O (5.00 mM) and Fe^{III}Cl₃ (0–5.0 mM) at pD 7.5 (A) and at pD 9.0 (B). (C) Concentrations of $U^{VI}O_2^{2+}$ /bihyat²⁻ species vs the added quantity of Fe^{III}Cl₃ based on the NMR spectra of (A, B). Labeling according to Scheme 2.

 $[V^{V}O_{2}(bihyat)]^{-}$ are 19.36 (6) and 17.87 (1), respectively),⁵² whereas the selectivity of the ligand to bind $U^{VI}O_{2}^{2+}$ in the $U^{VI}O_{2}^{2+}/VO_{4}^{3-}$ solutions increases at higher pDs.

 H_2 bihyat Binding of $U^{VI}O_2^{2+}$ in $U^{VI}O_2^{2+}/Fe^{III}$ Solutions by ¹H NMR Spectroscopy. In D_2O solutions containing $U^{VI}O_2^{2+}$, bihyat²⁻, and Fe^{III} the species 1, 2, 3, [Fe^{III}(bihyat)]⁺, and $[Fe^{III}(bihyat)_2]^-$ are formed (Scheme 4). The ¹H NMR spectra of D₂O solutions containing $[U^{VI}O_2(NO_3)_2(H_2O)_2] \cdot 4H_2O$ (5 mM), H₂bihyat (10.4 mM), and various quantities of Fe^{III}Cl₃ (0-5.00 mM) at pDs 7.5 and 9.0 are shown in Figure 8. The diagrams of the concentrations of the U^{VI}O₂²⁺ species versus the concentration of the added Fe^{III}Cl₃ at pDs 7.5 and 9.0 are also shown in Figure 6. The Fe^{III}-bihyat²⁻ complexes, namely, [Fe^{III}(bihyat)]⁺ and [Fe^{III}(bihyat)₂]⁻, are NMR-silent, and thus, the peaks in ¹H NMR spectra originate from $U^{VI}O_2^{2+}$ bihyat²⁻ complexes and the free H₂bihyat. The ¹H NMR spectrum of a D₂O solution containing $[U^{VI}O_2(NO_3)_2(H_2O)_2]$. $4H_2O(5.00 \text{ mM})$ and H_2 bihyat (10.4 mM) reveals the existence of the anion of 2 and the free ligand at both pDs. At pD 7.5 the stepwise addition of Fe^{III}Cl₃ to the solution results in the decrease of the anion of 2 and the free ligand and the increase of 1, that is, the D₂O solution containing 5.00 mM $U^{VI}O_2^{2+}/10.4$ mM H_2 bihyat/5.00 mM Fe^{III} contains 0.50 mM of the anion of 2 and 3.5 mM of 1, and 80% of the $U^{VI}O_2^{2+}$ is bound to bihyat²⁻, while at pD 9.0 the solution contains 3.40 mM of the anion of 2 and 1.60 mM of 1; 100% of the $U^{VI}O_2^{2+}$ is bound to bihyat²⁻. At pD > 10.5, bihyat^{2–} is entirely bound to $U^{VI}O_2^{2+}$ in the anion of **2**. Although Fe^{III} is released in solution at these high pD values (>7)

 $Fe(OH)_3$ does not precipitate from the solution, suggesting that interactions of $U^{VI}O_2{}^{2+}\text{-bihyat}{}^{2-}$ species with Fe^{III} keep it in solution.

H₂bihyat Binding of U^{VI}O₂²⁺ⁱn U^{VI}O₂²⁺/Fe^{III} Solutions by UV–Vis Spectroscopy. The UV–vis spectra of 2 (prepared from an aqueous solution containing 1.125 mM $[U^{VI}O_2(NO_3)_2(H_2O)_2]$ ·4H₂O and 2.270 mM H₂bihyat and characterized by ¹H NMR) at pH of 7.5 and 9.0 are shown in Figure S7. The spectra have a shoulder at 440 nm ($\varepsilon = 1100 \text{ M}^{-1}$ cm⁻¹, pH = 9.0; $\varepsilon = 1200 \text{ M}^{-1} \text{ cm}^{-1}$, pH = 7.5) and a long tail up to 700 nm.

The UV-vis spectra of the aqueous solutions containing $[U^{VI}O_{2}(NO_{3})_{2}(H_{2}O)_{2}]\cdot 4H_{2}O$ (1.125 mM), H₂bihyat (2.500 mM), and various concentrations of Fe^{III}Cl₃ (0-1.125 mM) at pH 7.5 and 9.0 are shown in Figures S9 and S10. The concentrations of the U^{VI}O₂²⁺ and Fe^{III} species were calculated by SQUAD, taking into account the uranium compounds 1, 2, and the iron(III) species $[Fe^{III}(bihyat)]^+$ and $[Fe^{III}(bihyat)_2]^-$. The speciation diagrams of the UVIO22+/bihyat2- and FeIII/ bihyat²⁻ species versus the concentration of the added Fe^{III}Cl₃ are shown in Figure S10. The anion of the dinuclear species 3 was not taken into account, because only negligible quantities are formed under these conditions, as it was evident by ¹H NMR spectroscopy. Most of the U^{VI}O₂²⁺ is bound to bihyat²⁻ at both pH values, but at pH 7.5 the major $U^{VI}O_2^{2+}$ species is complex 1, whereas at pH 9.0 it is the anion of 2, in agreement with the results obtained by ¹H NMR. Thus, it is evident on the basis of

both spectroscopies (NMR and UV–vis) that bihyat^{2–} prefers to ligate with $U^{VI}O_2^{2+}$ in alkaline $U^{VI}O_2^{2+}/Fe^{III}$ aqueous solutions.

CONCLUSIONS

In conclusion, a series of uranyl complexes with the bis-(hydroxylamino)triazine ligand H₂bihyat and various compositions of U^{VI}O₂²⁺/bihyat²⁻, depending on the molar ratio of $[U^{VI}O_2(NO_3)_2(H_2O)_2] \cdot 4H_2O/H_2$ bihyat, the solvent (water or acetonitrile), and the pHs, was synthesized. The X-ray structure analysis of the uranyl/bihyat^{2–} reveals very strong binding of bihyat^{2–}. Kinetic studies of $U^{VI}O_2^{2+}$ /bihyat^{2–} complexes in aqueous and organic solutions show that these complexes are in dynamic equilibrium with the ligation-deligation of bihyat²⁻ to be a slow process. The high strength of H₂bihyat to ligate to U^{VI}O₂²⁺ is demonstrated by its ability to displace from the equatorial plane other strong ligands, such as H2dipic and glutarimidedioxime, from the equatorial plane of $U^{VI}O_2^{2+}$. Thermodynamic (stability-selectivity) NMR and UV-vis studies show that H₂bihyat has a high affinity toward the $U^{VI}O_2^{2+}$ moiety and presents high selectivity to bind $U^{VI}O_2^{2+}$ in $U^{VI}O_2^{2+}/V^VO_4^{3-}$ and $U^{VI}O_2^{2+}/Fe^{III}$ solutions. The affinity of bihyat²⁻ for $U^{VI}O_2^{2+}$ increases by increasing the pH from 7 to 10. This is attributed to the large space around the equatorial plane of uranyl and the availability of the f-orbitals of the $U^{VI}O_2^{2+}$ to accommodate two strong ligands, in contrast to the smaller space of V^V and Fe^{III} ions.

We should also note that the BHT ligand H₂bihyat is (i) easily prepared, (ii) very stable in the atmosphere and water, (iii) inexpensive, and (iv) nontoxic. Thus, tridentate chelators, based on an N,N'-disubstituted BHT motif, represent very promising chelators for the detoxification of uranyl from biological organisms and sorbents for cheap and effective separation technologies of $U^{VI}O_2^{2+}$ from either wastes and groundwater or seawater.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00582.

1D and 2D NMR spectra, UV spectra, concentration of $U^{VI}O_2^{2^+}$ species versus the added quantity of Fe^{III}Cl₃, crystal data and structure refinement, bond lengths, bond angles (PDF)

Accession Codes

CCDC 1825543–1825546 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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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript

Notes

The authors declare no competing financial interest.

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