# Uranyl Complexes of Alkyl-Bridged Ditopic Diaminotetraphenol Ligands and Their Use as Uranyl Ion Extractors

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S Supporting Information

ABSTRACT: The coordination chemistry of uranyl ions was studied using long n-alkyl chain (n = 5−8) bridged by N,N,N',N'-tetrakis(2-hydroxy-3-methyl-5-$tert$-butylbenzyl)diaminoalkanes (H_4L1−H_4L4) as ligands. All ligands formed 2:1 (U-to-L ratio) complexes with uranyl ions, but in addition 1:1 complexes could be characterized using ligands H_4L2 and H_4L3. The complexes were characterized by elemental analysis, spectroscopy (IR and NMR), and X-ray diffraction. The 2:1 complexes are of two types: $[(UO_2)_2(H_2Lm)-(NO_3)_2(solvent)_2]$ (m = 1 and 2; solvent = ethanol or propanol) or $(cation)_2[(UO_2)_2(H_2Lm)(NO_3)_2(anion)_2]\cdot x solvent$ (m = 2 and 4; cation = triethylammonium, anion = nitrate or thiocyanate, and solvent = dichloromethane and acetonitrile; x = 1 or 2). The 1:1 complexes have the formula $[(UO_2)_2(H_2Lm)_2]$ (m = 2 and 3). In the solid state, 2:1 complexes are almost in a linear conformation with the uranyl ion at both ends of the ligand. The 1:1 complexes are cyclic dinuclear molecules. Preliminary studies of the ligands as uranyl ion extractors from water to dichloromethane were also performed. A high extraction efficiency was observed with H_4L3 for uranyl ions, and in the presence of Cu^{II}, Ni^{II}, Co^{II}, and Zn^{II} ions, a good extraction selectivity for uranyl ions was found with H_4L1.
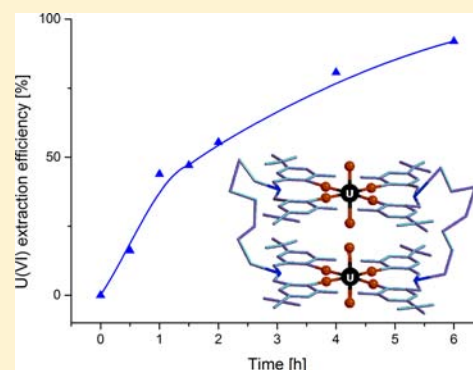
■ INTRODUCTION

Most of the world production of uranium is used in energy generation,[1] but applications for uranium in weapons, dyes,[1,2] and radiation shields[3−5] are known. Catalytic studies have also been made in which uranium complexes are used in the hydrogenation of alkenes and oligomerization, dimerization, hydrosilylation, and hydroamination of terminal alkynes.[6]

The interest in the chemistry of actinides (in particular, uranium, neptunium, and plutonium) is becoming more important as the need for uranium as an energy source is growing. This creates the need to improve the separation of these metals from the natural sources and to control their concentration in the environment. The recent Forum Article by Gorden et al. explicitly addresses these topics,[7] especially reminding us to further our fundamental understanding of the coordination chemistry of actinides to be able to develop new effective separation technologies.[7]

Effective extractors for uranium from low-concentration uranium sources, such as the secondary products of mines and even natural waters using octadecyl-bonded silica membrane disks modified with tri-n-octylphosphine oxide, have been reported.[8] One of the recent interesting results is the selective decontamination of real-world water samples from trace levels of uranium with a layered sulfide ion exchanger, $K_2MnSn_2S_6$.[9] The removal of poisonous uranium from the human body as metal−organic chelates is also an important topic.[10] In the current separation methods based on liquid−liquid extractions, one important problem is the extraction selectivity of uranium

from other hard Lewis acids, such as other actinides and lanthanides,[7] although soft ligands can also be used for uranyl ion separation.[9,11]

Liquid−liquid extraction of uranium is an extensively studied technique in which uranyl ions are extracted from an acidic water solution into an organic phase using specific ligands, such as alkylated phosphate ligands.[7] The commercially most interesting technique relies on the use of tri-n-butyl phosphate (TBP).[12−14] High loads of TBP are needed because it is used at up to 30 vol % of the organic phase rather than in a stoichiometric relation to the uranium ions.[15] In addition to the uranyl extraction methods reviewed in ref 7, for example, crown ethers[16,17] and bis(2-ethylhexyl) sulfoxides[18] have been used as ligands for this purpose. Also calixarenes, which are macrocyclic ligands with several phenolic groups, have been used in a study of uranium(VI) chemistry and extraction.[19]

Aminodiphenols have been extensively used as ligands in coordination chemistry, and their complexes have many practical applications.[20] Diaminotetraphenols are a new modification of aminodiphenols, and they are easy and inexpensive to prepare. Diaminotetraphenol can offer an ammine nitrogen and two phenolate oxygen atoms for metal-ion coordination at both ends of a flexible alkyl chain with possibilities open for forming linear or cyclic complexes (even different metal ions can occupy each end)[21] depending on the

Scheme 1. Schematic Representation of the Preparation of Uranyl Complexes 1−6
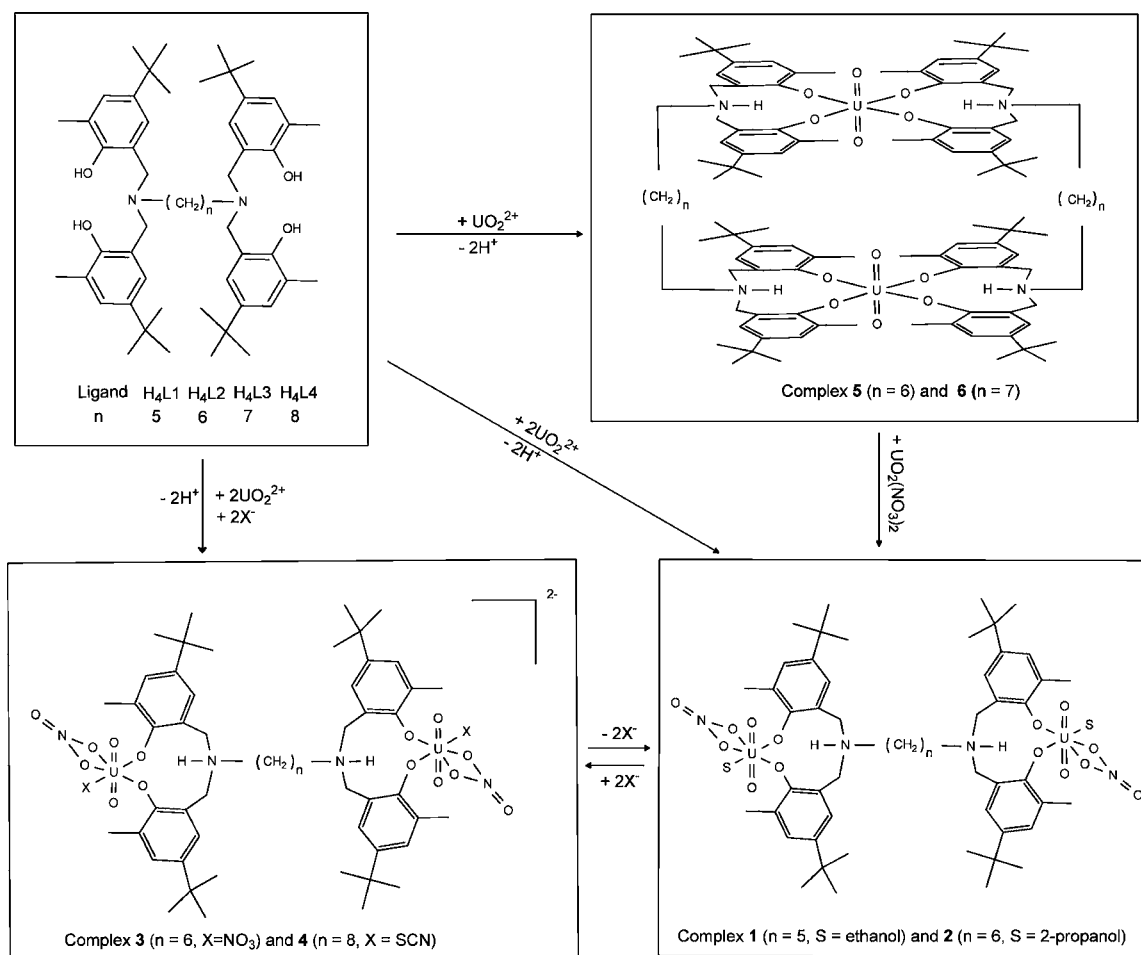
length of the bridge between nitrogen atoms (Scheme 1). The coordination sphere formed by these ligands is quite rigid, but the general shape of the complexes is flexible. The length of the long alkyl bridge can be easily modified, and suitable donor atoms can also be a part of the chain. Because diaminotetraphenols have only three donor atoms at both ends of the molecule, creating a possibility for labile ligands to fill the rest of the coordination sphere of the metal ions, the ligand is not able to bond to the metal ion at the same time. The steric and electronic properties of phenolate donor atoms can also be modified without major difficulties.

These ligands form complexes with transition-metal ions such as Cu^{II} [22] and $[MoO_2]^{2+}$.[23] Cu^{II} ions yield tetranuclear phenoxo complexes with interesting magnetic properties.[22] Dinuclear molybdenum(VI) complexes with diaminotetraphenols are linear, and they are active in oxo-transfer reactions[23] because one coordination position is filled by a labile solvent molecule. A structural study of titanium(IV), zirconium(IV), and hafnium(IV) complexes with similar ether-bridged ligands has recently been reported.[24] In general, very limited data of metal complexes with these types of ligands are available, but because of the fascinating results with these metals, we have extended our studies to the coordination chemistry of uranyl ions obtained with these ligands.

It has been shown earlier that uranyl ions form 1:1 and 1:2 (U-to-L) complexes with aminodiphenols.[25−29] These results show that the length of the alkyl chain in the aminodiphenols affects extraction of the uranyl ions from water to dichloro-

methane.[26] In this work, we report the coordination properties of n-alkyl-bridged (n = 5−8) diaminotetraphenols, namely, N,N,N′,N′-tetrakis(2-hydroxy-3-methyl-5-tert-butylbenzyl)-diaminoalkanes (H₄L1−H₄L4) toward uranyl ions (Scheme 1). We obtained three types of uranyl complexes with these ligands: 2:1 (U-to-L) (neutral and anionic) and neutral 1:1 complexes. The formed complexes were characterized by elemental analysis, spectral studies (IR and NMR), and X-ray diffraction. Finally, we report on preliminary studies on the extraction of uranyl ions from water to dichloromethane with these ligands. The extraction results are promising for effectiveness and selectivity.

■ EXPERIMENTAL SECTION

General Procedures. $UO_2(NO_3)_2 \cdot 6H_2O$ (p.a. grade, 98−102%) was purchased from Fluka. Acetonitrile-d_3 for NMR analyses was purchased from Euriso-top, and it contained 0.05% water that is visible in the ^1H NMR spectra. Other solvents of HPLC grade were purchased from commercial sources. Acetonitrile used in the syntheses was dried over activated 3 Å molecular sieves for at least 24 h prior to usage. All syntheses and extraction experiments were performed under an ambient laboratory atmosphere. The NMR spectra were recorded on a Bruker AVANCE DPX 500 FT-NMR spectrometer. The ^1H and ^{13}C NMR spectra for complexes 1−4 were recorded in CD_3CN and for complexes 5 and 6 in pyridine-d_5 at 30 °C. The chemical shifts are reported in parts per million and referenced internally using the residual polar solvent resonances relative to tetramethylsilane (CD_3CN, δ 1.94, ^1H NMR; δ 1.32, ^{13}C NMR; pyridine-d_5, δ 8.74, ^1H NMR; δ 150.5, ^{13}C NMR). Elemental analyses (C, H, and N) were

Table 1. Summary of the Crystallographic Data for Complexes 1−6

	1	2	3·2CH₂Cl₂	4·CH₃CN	5·4CH₂Cl₂	6·6CH₃CN
formula	$C_{57}H_{88}N_4O_{16}U_2$	$C_{60}H_{94}N_4O_{16}U_2$	$C_{68}H_{114}Cl_4N_8O_{20}U_2$	$C_{72}H_{117}N_9O_{14}S_2U_2$	$C_{112}H_{164}Cl_8N_4O_{12}U_2$	$C_{57}H_{88}N_4O_{16}U_2$
M_r	1561.37	1603.45	1981.53	1872.93	2518.13	2452.8
cryst syst	monoclinic	triclinic	monoclinic	triclinic	triclinic	triclinic
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	17.3675(4)	11.4371(3)	16.7441(3)	14.7010(3)	13.4717(3)	13.4360(3)
b (Å)	13.8639(3)	11.9448(4)	30.2719(6)	16.8936(3)	15.1909(3)	15.2076(4)
c (Å)	26.2164(7)	14.2944(4)	16.3369(3)	19.0443(4)	15.4542(3)	15.1051(5)
α (deg)	90	110.055(3)	90	79.6890(10)	103.1870(10)	98.8180(10)
β (deg)	96.6890(10)	100.201(2)	93.9390(10)	82.3500(10)	107.4660(10)	94.714(2)
γ (deg)	90	108.498(3)	90	64.4300(10)	91.5740(10)	95.312(2)
V (Å)	6269.4(3)	1647.60(10)	8261.2(3)	4189.25(14)	2921.58(10)	3022.23(14)
Z	4	1	4	2	1	1
D_c (g cm⁻³)	1.654	1.616	1.593	1.485	1.431	1.348
T (K)	123	173	123	123	123	123
μ(Mo Kα) (cm⁻¹)	5.226	4.974	4.114	3.972	3.008	2.736
no. of obsd reflns	6827	6477	16161	16373	11427	11852
R_{int}	0.043	0.029	0.032	0.038	0.044	0.041
no. of param	409	386	988	980	644	683
R1[a]	0.045 (0.031)[b]	0.026(0.022)	0.057 (0.036)	0.056 (0.037)	0.051 (0.041)	0.052 (0.039)
wR2[c]	0.060 (0.056)	0.051(0.049)	0.085 (0.077)	0.083 (0.075)	0.097 (0.092)	0.081 (0.077)

[a]R1 = $\sum ||F_o| - |F_c||/\sum|F_o|$. [b]Values in parentheses for reflections with $I > 2\sigma(I)$. [c]wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, where $P = (2F_c^2 + F_o^2)/3$.

performed using a Vario-El III elemental analyzer. The pH meter used was WTW INOLAB PH 720 with a WTW pH-electrode SENTIX81. Uranyl concentrations in extraction studies were determined using a PerkinElmer inductively coupled plasma optical emission spectroscopy (ICP-OES) Optima 8300 instrument. Crystallographic data for complexes **1** and **3−6** were collected with a Nonius-Kappa diffractometer equipped with a CCD area detector and for complex **2** with an Agilent Supernova diffractometer equipped with an Atlas area detector, using Mo Kα radiation ($\lambda = 0.71073$ Å). IR spectra were recorded on a Bruker Alpha platinum ATR spectrometer directly from the solid complexes (**1−6**).

Ligand Syntheses. The ligands were prepared according to ref 30.

Complex Syntheses. $[(UO_2)_2(H_2L1)(NO_3)_2(EtOH)_2]$ (**1**). $UO_2(NO_3)_2\cdot6H_2O$ (0.20 mmol, 100 mg) and H₄L1·2HCl (0.10 mmol, 88 mg) were dissolved in 5.0 mL of ethanol. NEt₃ (0.40 mmol, 52 μL) was added (we used less than the stoichiometric amount to avoid formation of a yellow precipitate). The reaction vessel was kept at room temperature for 24 h, after which **1** (red crystals) was collected by decantation and dried in air. Yield: 145 mg, 93%. ¹H NMR (CD₃CN, 500 MHz, ppm): 10.56 (s, 1.4H, N−H), 7.39 (s, 4H, aryl H), 7.08 (s, 4H, aryl H), 4.83 (d, 4H, N−CH₂-aryl), 3.96 (m, 4H, N−CH₂-aryl), 3.55 (m, 4H, CH₃−CH₂−OH, uncoordinated), 3.14 (m, 2H, CH₃−CH₂−OH, coordinated), 2.86 (s, 4H, N−CH₂-alkyl), 2.56 (s, 12H, aryl CH₃), 2.54 (s, 2.2H, EtOH), 2.19 (moisture), 1.26 (m, 40H, aryl-*t*Bu and alkyl CH₂), 1.12 (m, 9H, CH₃−CH₂−OH), 1.11 (m, 2H, alkyl CH₂). ¹³C NMR (CD₃CN, 126 MHz, ppm): 170, 142, 130, 129, 125, 121 (aryl C), 60.5 (EtOH), 58.0, 51.9 (N−CH₂-aryl), 48.0 (N−CH₂-alkyl), 34.4, 32.1 (aryl-*t*Bu), 23.9, (alkyl C), 18.7 (EtOH), 17.1 (aryl-CH₃), 9.17 (alkyl-C). IR: $\tilde{\nu}$ 3366 (s), 3079 (w), 2952 (s), 2866 (w), 1475 (s), 1262 (s), 1217 (s), 1024 (s), 902 (s), 772 (s), 519 (s) cm⁻¹. Elem anal. Calcd for $C_{57}H_{88}N_4O_{16}U_2$: C, 43.84; H, 5.68; N, 3.59. Found: C, 43.87; H, 5.81; N, 3.77.

$[(UO_2)_2(H_2L2)(NO_3)_2(2\text{-propanol})_2]$ (**2**). $UO_2(NO_3)_2\cdot6H_2O$ (0.040 mmol, 22 mg; used in excess to get a better yield) and **5**·4CH₂Cl₂ (0.020 mmol, 43 mg) were boiled in a mixture of 2.0 mL of MeCN and 1 mL of 2-propanol at 80 °C for 5 h. The dark-red crystals of **2** were collected by decantation and dried in air. Yield: 47 mg, 74%. ¹H NMR (CD₃CN, 500 MHz, ppm): 10.51 (s, 2H, N−H), 7.41 (s, 4H, aryl H), 7.11 (s, 4H, aryl H), 4.85 (d, 4H, N−CH₂-aryl), 3.97 (m, 4H, N−CH₂-aryl), 3.88 (m, 3H, H₃C−CHOH−CH₃), 2.94 (s, 4H, N−CH₂-alkyl), 2.59 (s, 12H, aryl CH₃), 2.49 (s, 3H, H₃C−CHOH−

CH₃), 2.19 (moisture), 1.29 (s, 36H, aryl *t*Bu), 1.17 (m, 4H, alkyl CH₂), 1.09 (d, 18H, H₃C−CHOH−CH₃), 0.75 (m, 4H, alkyl CH₂). ¹³C NMR could not be measured because of the low solubility of the compound. IR: $\tilde{\nu}$ 3203 (s), 3073 (w), 2957 (s), 2865 (w), 1475 (s), 1280 (s), 1257 (s), 877 (s), 768 (s), 518 (s) cm⁻¹. Elem anal. Calcd for $C_{60}H_{94}N_4O_{16}U_2$: C, 44.94; H, 5.91; N, 3.49. Found: C, 45.03; H, 6.38; N, 3.03.

$[HNEt_3]_2[(UO_2)_2(H_2L2)(NO_3)_2(NO_3)_2]\cdot2CH_2Cl_2$ (**3**·2CH₂Cl₂). $UO_2(NO_3)_2\cdot6H_2O$ (0.20 mmol, 100 mg) and H₄L2 (0.10 mmol, 82 mg) were dissolved in 2.0 mL of a CH₂Cl₂−MeCN (1:1) mixture. Activated molecular sieves (3 Å) were added, the solution was dried for 3 h, and 0.20 mmol of NEt₃ in 5.0 mL of CH₂Cl₂ was added. Drying was continued for 21 h. A total of 3.0 mL of *n*-heptane was added, and after 20 min, the solution was centrifuged to remove formed solid and the molecular sieves. A total of 1 mL more of heptane was added, and the uranium solution was kept for 24 h in a refrigerator (6 °C). Formed red crystals of **3** were separated by decantation and dried in air. Yield: 45 mg, 25%. ¹H NMR (CD₃CN, 500 MHz, ppm): 10.6 (m, 0.2H, N−H), 8.32 (m, 2.2H, N−H), 7.40 (s, 4H, aryl H), 7.10 (s, 4H, aryl H), 4.81 (s, 4H, N−CH₂-aryl), 3.93 (s, 4H, N−CH₂-aryl), 3.11 (m, 14H, HN(CH₂−CH₃)₃), 2.93 (s, 4H, N−CH₂-alkyl), 2.59 (s, 12H, aryl CH₃), 2.26 (moisture), 1.26 (m, 36H + 4H + 21H, aryl *t*Bu, alkyl CH₂, HN(CH₂−CH₃)₃), 0.78 (m, 4H, alkyl CH₂). Elem anal. Calcd for **3**, $C_{66}H_{110}N_7O_{20}U_2$: C, 44.09; H, 6.17; N, 5.45. Found: C, 43.76; H, 6.03; N, 6.18. IR: $\tilde{\nu}$ 3058 (w), 2951 (m), 2864, 1475 (s), 1261 (s), 1217 (s), 1025 (s), 889 (s), 769 (s), 521 (s) cm⁻¹.

$[HNEt_3]_2[(UO_2)_2(H_2L4)(NO_3)_2(SCN)_2]\cdot MeCN$ (**4**·MeCN). $UO_2(NO_3)_2\cdot6H_2O$ (0.10 mmol, 50 mg) was dissolved in 1.0 mL of EtOH. H₄L4 (0.050 mmol, 42 mg) was dissolved in 1.0 mL of CH₂Cl₂. The solutions were mixed and heated until total dissolution. Then the solution was cooled to room temperature, and [NH₄][SCN] (0.10 mmol, 7.6 mg) dissolved in 0.75 mL of EtOH and 0.1 mmol (14 μL) of NEt₃ were added. The solution was made more nonpolar by adding 2.0 mL of hexane to speed up crystallization. The capped vessel was kept for 18 h at room temperature. Formed red crystals were separated mechanically and washed twice with a small amount of diethyl ether. Yield: 47 mg, 51%. ¹H NMR for **4** (CD₃CN, 500 MHz, ppm): 11.12 (s, 2H, N−H), 7.40 (s, 4H, aryl H), 7.12 (s, 4H, aryl H), 4.79 (d, 4H, N−CH₂-aryl), 3.95 (m, 4H, N−CH₂-aryl), 3.12 (q, 12H, HNCH₂CH₃), 2.97 (s, 4H, alkyl CH₂), 2.65 (d, 12H, aryl CH₃),

2.13 (moisture), 1.30 (m, 36H + 4H, aryl tBu and alkyl CH_2 (overlapping)), 1.24 (t, 18H, $HNCH_2CH_3$), 0.94 (m, 4H, alkyl CH_2), 0.77 (m, 4H, alkyl CH_2).^{13}C NMR could not be measured because of the low solubility of the compound. Elem anal. Calcd for **4**, $C_{70}H_{114}N_8O_{14}S_2U_2$: C, 45.9; H, 6.27; N, 6.12. Found: C, 45.3; H, 6.11; N, 6.10. IR: $\tilde{\nu}$ 3060 (w), 2953 (s), 2863 (w), 2050 (s), 1479 (s), 1268 (s), 1218 (s), 887 (s), 765 (s), 523 (s) cm^{-1}

[(UO₂)₂(H₂L2)₂]·4CH₂Cl₂ (5·4CH₂Cl₂). $UO_2(NO_3)_2\cdot6H_2O$ (0.40 mmol, 200 mg) and H₄L2 (0.40 mmol, 330 mg) were dissolved in 18.0 mL of CH_2Cl_2–MeCN (2:1) by boiling. The solution was cooled to room temperture, and NEt₃ (~0.9 mmol, 120 μL) was added and kept for 24 h at room temperature. The orange crystals of **5·4CH₂Cl₂** were separated, washed with 5.0 mL of CH_2Cl_2 and 5 mL of H_2O, and dried in air. Yield: 380 mg, 87%. (Single crystals for X-ray analysis were prepared in a $^1/_4$ scale of starting materials in a narrow class tube using 9 mL of a 2:1 CH_2Cl_2–MeCN solution.) ^{1}H NMR (pyridine-d_5, 500 MHz, ppm): 10.86 (s, 2H, N–H), 7.55 (m, 4H, aryl H), 7.25 (d, 4H, aryl H), 5.68 (CH_2Cl_2), 5.48 (q, 2H, N–CH_2-aryl), 4.9 (moisture), 4.55 (q, 2H, N–CH_2-aryl), 3.96 (d, 4H, N–CH_2-aryl), 3.45 (m, 2H, N–CH_2-alkyl), 2.56 (m, 2H, N–CH_2-alkyl), 2.47, 2.33 (s, 6H + 6H, aryl CH_3), 1.83 (m, 2H, alkyl CH_2), 1.54 (m, 2H, alkyl CH_2), 1.47, 1.38 (m, 18H + 18H, aryl tBu), 1.03 (m, 2H, alkyl CH_2), 0.70 (m, 2H, alkyl CH_2). ^{13}C NMR (pyridine-d_5, 126 MHz, ppm): 165, 153, 141, 139, 127, 126 (aryl C), 60.4, 55.4 (N–CH_2-aryl), 53.3, 50.5 (N–CH_2-alkyl), 33.7, 33.5, 32.1, 31.5 (aryl tBu), 27.5, 27.3, 27.2, 26.1, 20.3 (alkyl C), 16.7, 16.5 (aryl CH_3). IR: $\tilde{\nu}$ 3045 (w), 2959 (s), 2862 (w), 1472 (s), 1267 (s), 1216 (s), 1124 (s), 862 (s), 833 (s), 513 (s) cm^{-1}. Elem anal. Calcd for $C_{108}H_{156}N_4O_{12}U_2$: C, 59.5; H, 7.22; N, 2.57. Found: C, 59.2; H, 6.94; N, 2.52.

[(UO₂)₂(H₂L3)₂]·6MeCN (6·6MeCN). $UO_2(NO_3)_2\cdot6H_2O$ (0.20 mmol, 100 mg) was dissolved in 5.0 mL of MeCN. H₄L3·2HCl (0.20 mmol, 182 mg) and NEt₃ (0.90 mmol, 120 μL) were dissolved in 5.0 mL of tetrahydrofuran. The solutions were mixed until a red solution was obtained. After 18 h, **6** was collected as orange crystals. Yield: 162 mg, 70%. ^{1}H NMR (pyridine-d_5, 500 MHz, ppm): 7.52 (s, 4H, aryl H), 7.25 (s, 4H, aryl H), 5.47 (q, 2H, N–CH_2-aryl), 5.0 (moisture), 4.47 (q, 2H, N–CH_2-aryl), 3.98 (d, 4H, N–CH_2-aryl), 3.67 (m, 2H, N–H) 3.43 (m, 2H, N–CH_2-alkyl), 2.61 (m, 2H, N–CH_2-alkyl), 2.47, 2.33 (d, 6H + 6H, aryl CH_3), 1.70 (m, 4H, alkyl CH_2), 1.53 (m, 2H, alkyl CH_2, overlapping), 1.46, 1.38 (m, 18H + 18H, aryl tBu, 2H alkyl CH_2 overlapping), 1.00 (m, 4H, alkyl CH_2), 0.66 (m, 2H, alkyl CH_2). ^{13}C NMR (pyridine-d_5, 126 MHz, ppm): 167, 155, 143, 141, 129, 127 (aryl C), 62.3, 57.5 (N–CH_2-aryl), 55.2, 52.3 (N–CH_2-alkyl), 35.6, 35.5, 34.0, 33.4 (aryl tBu), 31.4, 29.3, 29.1, 27.4, 20.69 (alkyl C), 18.7, 18.5 (aryl CH_3). IR: $\tilde{\nu}$ 2953 (s), 2863 (m), 1476 (s), 1271 (s), 1218 (s), 1025 (m), 857 (s), 830 (s), 769 (s), 513 (s) cm^{-1}. Elem anal. Calcd for $C_{116}H_{169}N_7O_{12}U_2$: C, 59.9; H, 7.31; N, 2.54. Found: C, 59.9; H, 7.33; N, 2.46.

X-ray Crystallography. The crystal data for compounds **1**–**6** are summarized in Table 1 along with other experimental details. The crystallographic data for **1** and **3**–**6** were collected at 123 K with an Enraf Nonius-Kappa CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were collected using φ and ω scans, and they were processed with *DENZO-SMN v0.93.0*.[31] Absorption corrections were applied for compounds **1** and **3**–**6** with *SADABS*.[32]

For complex **2**, the data were collected with an Agilent SuperNova dual-wavelength diffractometer equipped with an Atlas CCD area detector with Mo Kα radiation (λ = 0.71073 Å) using a *CrysAlisPro* program package.[33] The empirical absorption correction for **2** was made with a *SCALE3 ABSPACK* scaling algorithm, as implemented in the *CrysAlisPro* program.

The structures were solved by direct methods using the *SHELXS-97*[34] program or the *SIR-97*[35] program, and the full-matrix least-squares refinements on F^2 were performed using the *SHELXL-97*[34] program. The figures were drawn with *ORTEP-3* for Windows.[36] For all compounds, the heavy atoms were refined anisotropically. The CH hydrogen atoms were included at the calculated distances with fixed displacement parameters from their host atoms (1.2 or 1.5 times those

of the host atom). The OH hydrogen atoms were located from the electron density map and refined isotropically.

Extraction. Uranyl ion extraction from water to CH_2Cl_2 was studied in three separate experimental sets, I–III.

I. Effect of the Initial pH. The uranyl ion solution (12.5 mM) was extracted into CH_2Cl_2 with ligand H₄L3 at four different pH values (2.8, 4.0, 5.0, and 5.7). The uranyl sample at pH 2.8 was prepared by dissolving 0.050 mmol of $UO_2(NO_3)_2\cdot6H_2O$ in 4.0 mL of water in a 10 mL test tube. A total of 0.050 mmol of H₄L3·2HCl was dissolved in 4 mL of CH_2Cl_2, neutralized with 0.11 mmol of 6 M NH₄OH, and added to the uranyl solution. The sample at pH 4.0 was prepared by dissolving 0.050 mmol of $UO_2(NO_3)_2\cdot6H_2O$ in 3.0 mL of water. The pH was adjusted to 4.0 using 6 M NH₄OH and the volume to 4.0 mL with water. The neutralized H₄L3·2HCl in 4 mL of CH_2Cl_2 was added as in pH 2.8. The samples at pH 5.0 and 5.7 were prepared similarly to the sample at pH 4.0.

The test tubes in the pH experiments were mixed for 6 h. Samples were taken from water and CH_2Cl_2 phases at 0, 0.5, 1, 1.5, 2, 4, and 6 h. The uranium contents of the water and CH_2Cl_2 phases were separately monitored.

Samples of 50 μL were taken from the water phase into 10 mL volumetric flasks. The uranyl ion contents were analyzed with an ICP-OES instrument at 385.958 nm using axial measurement. The 50 μL samples taken from the CH_2Cl_2 phase were placed into 10 mL volumetric flasks and allowed to dry. The dry samples were heated for 10 min with 500 μL of dilute HNO₃ (~1.4 M HNO₃) at 90 °C. The solutions obtained were filtered through 45 μm Supor (PES) membrane syringe filters to remove the organic solid before ICP-OES analysis.

II. Extraction Efficiency. The extraction efficiency of H₄L1, H₄L2, and H₄L4 was investigated at pH 5.7 using the procedure for H₄L3. From the CH_2Cl_2 phase of H₄L3 extraction, crystals were obtained with the cell parameters of a = 12.2485 Å, b = 15.6378 Å, c = 15.5739 Å, α = 80.57°, β = 81.88° γ = 87.54°, and V = 2914.7 Å^3, which suggests that uranium(VI) is extracted as **5·4CH₂Cl₂**.

III. Uranyl Ion Selectivity. These experiments with H₄L1, H₄L2, H₄L3, and H₄L4 at pH 5.5 were similarly to experiment II, but at the beginning, 0.050 mmol of $Cu(NO_3)_2\cdot6H_2O$, $Zn(NO_3)_2\cdot4H_2O$, $Co(NO_3)_2\cdot6H_2O$, and $Ni(NO_3)_2\cdot6H_2O$ were added into the 3.5 mL water solution containing the uranyl ions. Because of the acidity of the ions, more ammonia had to be used (0.15 mmol) to keep the pH at 5.50 in the beginning. The amount of the ligands was reduced to 0.050 mmol. This reaction was followed for 4 h.

Uranyl Separation and Ligand Recovery from Complex 6. Complex **6** was decomposed with concentrated HCl in methanol. After decomposition, ligand H₄L3·2HCl was precipitated by adding water to the methanol solution (yield 79%). Residual uranium was removed by recrystallization from a MeOH–water mixture in the presence of HCl. Details of the process are described in the Supporting Information.

■ RESULTS AND DISCUSSION

Syntheses. Ligands H₄L1–H₄L4 were prepared using our recently reported synthetic method.[30] Six new ditopic uranium-(VI) complexes were isolated from the reactions of $UO_2(NO_3)_2\cdot6H_2O$ with H₄L1–H₄L4 ligands (Scheme 1) and were characterized by elemental analysis, IR and NMR spectroscopy, and X-ray diffraction. Four complexes formed had a U-to-L ratio of 2:1 with a linear ligand conformation. **1** and **2** had the formula $[(UO_2)_2(H_2Lm)(NO_3)_2(solvent)_2]$ (m = 1 and 2; solvent = ethanol or isopropyl alcohol) and **3** and **4** are anionic complexes with the formula $(cation)_2[(UO_2)_2(H_2Lm)(NO_3)_2(anion)_2]\cdot x$solvent ($m$ = 2 or 4, cation = triethylammonium, anion = nitrate or thiocyanate, x = 1 or 2, and solvent = dichloromethane or acetonitrile). **5** and **6** are 1:1 complexes of the form $[(UO_2)_2(H_2Lm)_2]$ (m = 2 and 3) with a cyclic structure.

We had demonstrated earlier that the metal complexes of ditopic diaminotetraphenols often crystallize with solvent adducts.[22,23] These ligands tend to leave cavities while forming solid-state structures. In order to obtain good crystals of these complexes, one should find suitable "fillings" for those cavities; it has also been a challenge in this work. Several of the complexes can form simultaneously when the syntheses are performed in single solvents, such as alcohols (methanol, ethanol, and isopropyl alcohol), acetonitrile, and dichloromethane, varying the stoichiometry of the uranyl ion, ligand, and base. On the other hand, the 2:1 complexes are more soluble in MeCN than the 1:1 complexes. In CH_2Cl_2, the solubility is the reverse. Different solubilities of the starting materials cause difficulties in the preparation of pure complexes. Therefore, we have used mixtures of the above solvents in many syntheses in order to minimize unwanted side products.

In the syntheses of the 2:1 complexes, the amount of base is crucial, and the most effective procedure was to use a smaller amount of base than suggested by the stoichiometry. The difficulty with the base can be eliminated by preparing first the 1:1 complex (**5** or **6**), which forms easily, and then the ring in the complex is opened in an alcohol solution in the presence of uranyl nitrate. Methanol, ethanol, and isopropyl alcohol were tested as solvents and found to be suitable while boiling. The best quality crystals for **2** were formed in isopropyl alcohol. The ring does not open in an acetonitrile or CH_2Cl_2 solution, indicating that an acidic proton must be present and the mere presence of water in uranyl nitrate is unable to open the ring.

X-ray Diffraction Analysis. 1 crystallizes in the monoclinic space group $C2/c$, whereas $[(UO_2)_2(H_2L2)(NO_3)_2(i\text{-}PrOH)_2]$ (**2**) crystallizes in a triclinic space group $P\bar{1}$. The asymmetric unit of **1** contains half of the molecule, and in the whole molecule, there is a 2-fold axis (Figure 1). The asymmetric unit
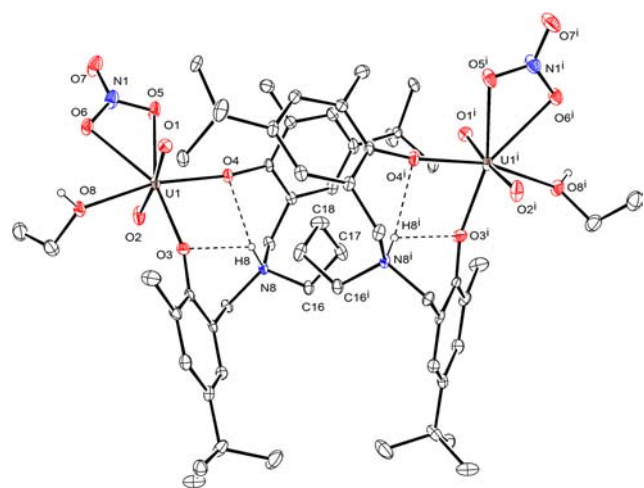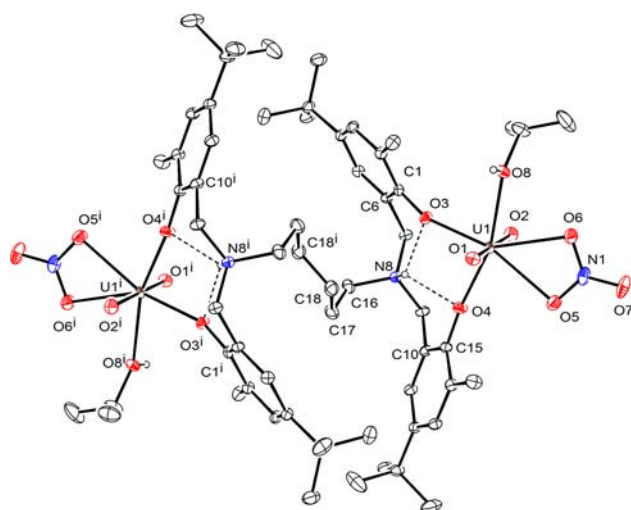

Figure 1. Molecular structure of **1**. Thermal ellipsoids have been drawn at the 20% probability level. CH hydrogen atoms are omitted for clarity.

of **2** also contains half of the molecule, which has an inversion center (Figure 2). In both compounds, the alkyl chain between N8 and N8^i is twisted. The coordination environment around the uranium(VI) nucleus is similar in both complexes and is a distorted pentagonal bipyramid. In both complexes, the coordination environment around the uranium(VI) nucleus is of the type $UO_2(O_{phenoxido})_2(O_{nitrato})_2(O_{alcohol})$. A similar coordination sphere around uranium is found in uranyl

Figure 2. Molecular structure of **2**. Thermal ellipsoids have been drawn at the 20% probability level. CH hydrogen atoms are omitted for clarity.

aminodiphenolate in which alcohol has been replaced by water.[29] The pentagon around the O=U=O moiety is formed from two phenoxo ligands that occupy the cis positions, two oxygen atoms from the didentate nitrate anion, and the oxygen atom from the alcohols. Selected bonding parameters for **1** and **2** are presented in Table 2. The bonding parameters around uranium in **1** and **2** are quite similar to those in ref 29.

The O1=U1=O2 angles are slightly distorted from 180° [173.5(1)° for **1** and 174.8(1)° for **2**], and the oxo atoms are pointing toward the nitrato group. The bond distances and angles are within the normal range.[37] In **2**, there is a long U=O bond compared to the others; the U1=O1 bond length is 1.800(2) Å and U1=O2 is 1.774(2) Å, and in **1**, they are 1.772 and 1.774(3) Å, respectively. The reason for the long U1=O1 bond in **2** is formation of the hydrogen bond (O8H···O1=U1).

One can expect that the long CH_2 chains containing a ditopic ligand could form complexes where the ligand has a linear conformation. $Mo^{VI}O_2$ compounds with similar ligands are quite linear.[23] In the solid-state structures of **1** and **2**, we find that the alkyl chains are not linear and are twisted so that the two uranyl cations come quite close to each other. The twist can be due to the hydrogen bonds and other packing effects that stabilize the solid-state structures **1** and **2**.

In both complexes and also in the rest of the compounds reported in this paper, there are weak bifurcated intramolecular hydrogen bonds from H8 to O3 and O4. In **1**, intermolecular hydrogen bonds are formed from the OH hydrogen atom of ethanol to the nitrate oxygen atom of the neighboring molecule, with the nitrate oxygen atom accepting an OH hydrogen atom from the same neighboring molecule (Figure S1 in the Supporting Information). These double-bridging hydrogen bonds bind the molecules to the chains. The chains are joined by a weak C16H···O hydrogen bond and van der Waals forces, forming a three-dimensional net. In **2**, intermolecular OH···O=U hydrogen bonds are formed (Figure S2 in the Supporting Information). However, now there are two weak C9H···O and C20H···O (the carbon atom from the *tert*-butyl group) hydrogen bonds, which form chains joining the molecules to a layer-type structure.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1−6

	1	2	3·2CH$_2$Cl$_2$	4·CH$_3$CN	4·CH$_3$CN^a	5·4CH$_2$Cl$_2$	6·6CH$_3$CN
U1=O1	1.772(3)	1.800(2)	1.783(4)	1.777(4)	1.781(4)	1.798(3)	1.804(3)
U1=O2	1.774(3)	1.774(2)	1.786(4)	1.791(4)	1.780(4)	1.809(3)	1.804(3)
U1−O3	2.200(3)	2.217(2)	2.222(3)	2.195(3)	2.196(3)	2.251(3)	2.246(3)
U1−O4	2.198(2)	2.176(2)	2.201(3)	2.213(3)	2.223(3)	2.253(3)	2.273(3)
U1−O5	2.552(3)	2.546(2)	2.529(4)	2.542(4)	2.568(4)	2.258(3)^b	2.220(3)^b
U1−O6	2.560(3)	2.551(2)	2.540(4)	2.552(3)	2.563(4)	2.238(3)^c	2.284(3)^c
U1−O8/N2^d	2.457(3)	2.446(2)	2.501(3)	2.480(4)^d	2.469(4)^d		
O1=U1=O2	173.53(13)	174.75(10)	173.02(16)	174.76(15)	174.00(16)	179.20(17)	178.61(13)
O3−U1−O4	82.98(10)	84.01(8)	83.19(13)	83.16(12)	84.29(12)	84.17(12)	84.49(11)
O3−U1−O5	158.33(10)	161.48(8)	161.92(12)	160.76(13)	161.52(12)	95.22(12)^b	96.13(11)^b
O3−U1−O8/N2^d	82.42(10)	80.90(8)	79.14(12)	79.63(13)^d	80.62(14)^d		
O4−U1−O5	75.57(9)	77.73(9)	78.80(12)	77.67(13)	77.25(12)	97.08(13)^b	94.33(11)^b
O4−U1−O8/N2^d	165.33(10)	163.80(9)	162.23(13)	162.53(13)^d	164.63(14)^d		
O5−U1−O6	50.00(9)	49.83(8)	50.47(12)	50.15(13)	49.69(12)	83.40(13)^{b,c}	85.06(11)^{b,c}
O5−U1−O8/N2^d	119.09(10)	117.58(8)	118.80(12)	119.59(14)^d	117.76(14)^d		
O6−U1−O8/N2^d	69.09(10)	67.92(8)	68.42(12)	69.45(14)^d	68.18(14)^d		
C1−O3−U1	163.3(3)	157.0(2)	156.9(3)	167.8(3)	172.4(3)	161.0(3)	152.9(3)
C15−O4−U1	171.5(2)	172.4(2)	158.2(3)	167.8(3)	150.0(3)	162.2(3)	132.5(2)
C21−O5−U1						162.1(3)^b	168.3(3)^b
C35−O6−U1						167.3(3)^c	146.9(3)^c

^{a}The parameters at the other end of the molecule, such as U2−O11, U2−O12, and so on. ^{b}O5^i; i = inversion operation. ^{c}O6^i. ^{d}In compound **6**, N2 in the position of O8.

Compounds **3**·2CH$_2$Cl$_2$ and **4** crystallize in the space group P1̄. Compound **3**·2CH$_2$Cl$_2$ has the formula [HNEt$_3$]$_2$[(UO$_2$)$_2$-(H$_2$L2)(NO$_3$)$_2$(NO$_3$)$_2$]·2CH$_2$Cl$_2$. The structure of the anionic part, [(UO$_2$)$_2$(H$_2$L2)(NO$_3$)$_2$(NO$_3$)$_2$]$^{2-}$, is centrosymmetric and similar to that of molecules **1** and **2** except that the coordinated solvent molecule is now replaced by a nitrate group (Figure 3). The coordination geometry around the uranium atom is a distorted pentagonal bipyramid in which there are in the xy plane two cis-positioned phenoxides, a didentately coordinated nitrate, and a monodentate nitrate. The uranyl ion and p-methyl-N-benzyltetrahomodiazacalix[4]arene form a mononuclear complex with a similar coordination

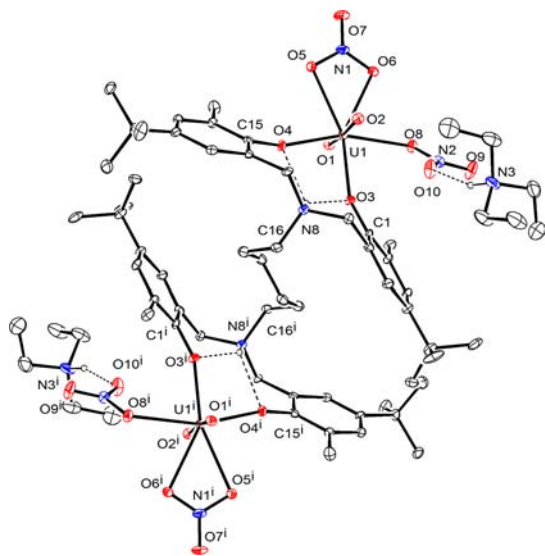sphere around uranium.[38] The uranyl oxo atoms are, of course, in the trans position above and below the pentagonal xy plane. The bond lengths are similar to those of **1** except for the U−O8$_{nitrate}$ distance, which is slightly longer [2.501(3) Å for **3**·2CH$_2$Cl$_2$, and U−O8$_{alcohol}$ = 2.457(3) Å for **1**]. This lengthening can be understood by the weaker bonding ability of the nitrate oxygen atom versus an alcohol oxygen atom. The negative charges of the anionic complex unit are balanced by two triethylammonium cations, which form hydrogen bonds to the monodentate nitrates.

Compound **4**·CH$_3$CN has the formula [HNEt$_3$]$_2$[(UO$_2$)$_2$-(H$_2$L4)(NO$_3$)$_2$(SCN)$_2$]·CH$_3$CN (Figure 4). The noncentro-symmetric structure of the anionic part of **4**·CH$_3$CN is similar

Figure 3. Structure of **3**·2CH$_2$Cl$_2$. Thermal ellipsoids have been drawn at the 20% probability level. CH$_2$Cl$_2$ molecules and CH hydrogen atoms are omitted for clarity.
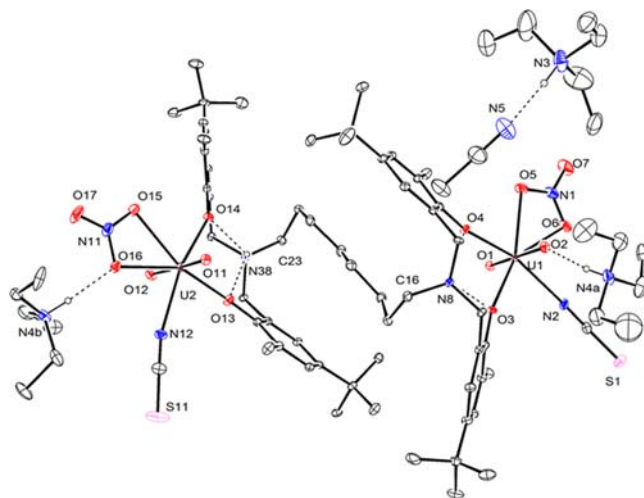

Figure 4. Structure of **4**·CH$_3$CN. Thermal ellipsoids have been drawn at the 20% probability level. CH hydrogen atoms are omitted for clarity. Triethylammonium cations (the central nitrogen atoms labeled as N4a and N4b) are disordered over two positions in a 1:1 ratio.

to that of **3**·2CH$_2$Cl$_2$, but now the coordinated anions are thiocyanides, which occupy the place of the monodentate nitrate groups, producing UO$_2$(O$_{phenoxido}$)$_2$(O$_{nitrato}$)$_2$-(N$_{thiocyanato}$)-type coordination spheres for the uranium atoms at both ends of the ligand. The nitrogen atoms N8 and N38 are protonated, and the extra negative charges are also balanced by the triethylammonium cations. The bond lengths are very similar in **4**·CH$_3$CN and **3**·2CH$_2$Cl$_2$. The U1−N bond lengths, 2.480(4) and 2.469(4) Å, in **4**·CH$_3$CN are shorter than the corresponding U1−O8 length of 2.501(3) Å in **3**·2CH$_2$Cl$_2$ because N$_{thiocyanato}$ is normally a more strongly coordinating atom than O$_{nitrato}$.

One of the two triethylammonium ions included in the unit cell forms a hydrogen bond to an acetonitrile molecule. The other [HNEt$_3$]$^+$ ion is, however, disordered and can be found in two places, as indicated by the cations with the labels N4a and N4b in a 1:1 ratio in Figure 4. The formed hydrogen bonds are either from N4a to O2$_{oxo}$ or from N4b to O16$_{nitrato}$. Uranyl complexes in which nitrate and thiocyanate groups are simultaneously coordinated to the uranyl ion are rare, and only one has been previously reported.[39]

If the chain length of the alkyl bridge of the ligand is appropriate, as in H$_4$L2 and H$_4$L3, novel zwitterionic cyclic 1:1 complexes (U-to-L) are formed. Compounds **5**·4CH$_2$Cl$_2$ (Figure 5) and **6**·6CH$_3$CN (Figure 6) are actually dinuclear
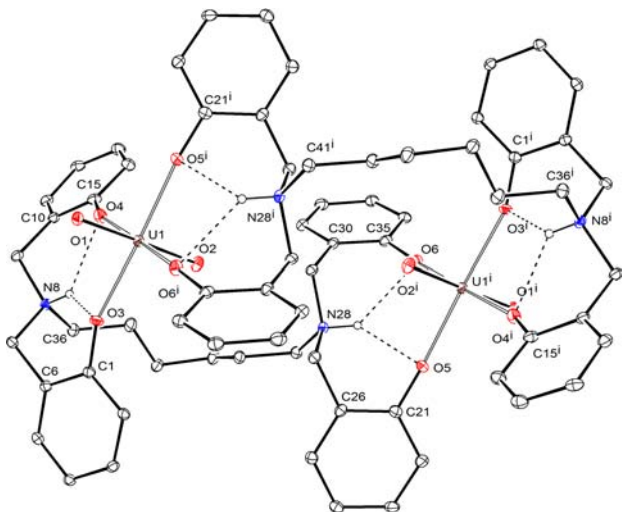

Figure 5. Molecular structure of **5**·4CH$_2$Cl$_2$. Thermal ellipsoids have been drawn at the 20% probability level. CH$_2$Cl$_2$ molecules, methyl and *tert*-butyl substituents of the aromatic ring, and CH hydrogen atoms are omitted for clarity. Note the different atom labeling compared to that in compounds **1**−**4**.

rings (Figures 5 and 6). The coordination spheres around the uranyl ions are quite similar in both complexes. In the complexes, the oxygen donor atoms are in a distorted octahedral geometry around the uranium(VI) atom. The coordination environment is of the type UO$_2$(O$_{phenoxido}$)$_4$ with U−O single bonds from 2.238(3) to 2.358(3) Å in **5** and from 2.220(3) to 2.373(3) Å in **6**. Similar coordination spheres around uranium(VI) can be found in a zwitterionic uranyl complex with *p*-methyl-*N*-benzyltetrahomodiazacalix[4]-arene (the U−O bonds are from 2.248 to 2.285 Å)[40] and in a cationic uranyl complex with bis(homooxa)-*p*-*tert*-butylcalix-[4]arene (U−O bonds from 2.248 to 2.276 Å).[41] Macro-molecular cyclic rings with similar dimethyl-substituted
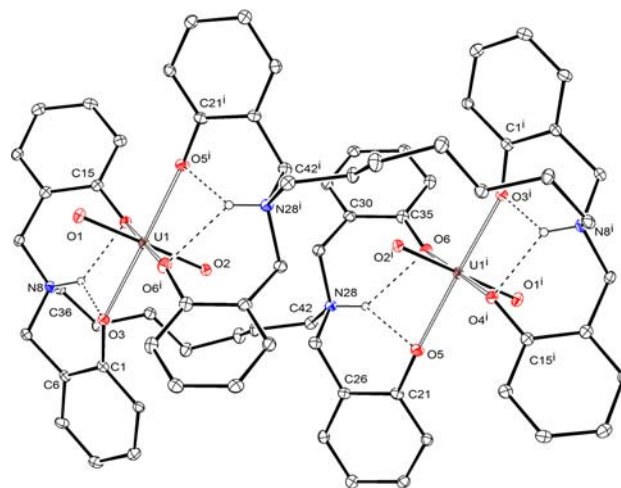

Figure 6. Molecular structure of **6**·6CH$_3$CN. Thermal ellipsoids have been drawn at the 20% probability level. CH$_3$CN molecules, methyl and *tert*-butyl substituents of the aromatic ring, and CH hydrogen atoms are omitted for clarity. The atom labeling is the same as that for **5**·4CH$_2$Cl$_2$.

diaminotetraphenols have been prepared earlier with Cu^{II} ions;[20] however, these have a 2:1 (Cu-to-L) composition with two phenoxido bridges. Two cyclic molecules of the uranyl ion with a 1:1 U-to-L ratio have been reported but with different types of ligands.[42−44]

In compounds **5**·4CH$_2$Cl$_2$ and **6**·6CH$_3$CN, the phenoxo atoms from two different [H$_2$L2]$^{2−}$ (in **5**·4CH$_2$Cl$_2$) and [H$_2$L3]$^{2−}$ (in **6**·6CH$_3$CN) ligands are in the trans position to each other. The structural parameters in both complexes are quite similar: especially for the U−O bonds (Table 1), which are almost the same at the 3σ level. The largest angular differences between **5**·4CH$_2$Cl$_2$ and **6**·6CH$_3$CN are related to the orientation of the neighboring phenoxo groups, which is indicated by the angles O3−U1−O6^i (95.2° for **5**·4CH$_2$Cl$_2$ and 96.1° for **6**·6CH$_3$CN) and O4−U1−O5^i (97.08° for **5**·4CH$_2$Cl$_2$ and 94.3° for **6**·6CH$_3$CN).

The greatest difference can be found in the U−O$_{phenoxo}$−C$_{aryl}$ angles, which vary from 161.0(3)° to 167.3(3)° in **5**·4CH$_2$Cl$_2$ and from 132.5(2)° to 168.3(3)° in **6**·6CH$_3$CN. For example, the U1−O4−C15 angle is 162.2(3)° for **5**·4CH$_2$Cl$_2$ and 132.5(2)° for **6**·6CH$_3$CN. This ∼30° difference in the angles is a clear demonstration that the length of the flexible alkyl chain can influence the coordination sphere of an uranyl ion; if the size of the chain is not suitable, these 1:1 complexes do not form. So far, we have not succeeded in preparing similar U-to-L (1:1) compounds in the solid state with H$_4$L1 or H$_4$L4, although we have made several attempts. The 1:1 complexes are rigid in solution so that in their ^{1}H NMR spectra even the methyl and *tert*-butyl groups are separated into two patterns, and separate and broad proton signals of the alkyl bridges are also seen.

In **5**·4CH$_2$Cl$_2$, the cyclic units bind together via weak CH···O═U hydrogen bonds and van der Waals forces while dichloromethane molecules fill the space between the cyclic molecules. The crystal packing forces influence the (CH$_2$)$_n$ bridges, and this modifies the bond angles near the uranium center but does not cause large modifications in the bond angles around the uranium atom. In **6**·6CH$_3$CN, the structure is stabilized via weak CH···O═U hydrogen bonds and CH···N (acetonitrile) hydrogen bonds.

Extraction Studies. Separation of the uranyl ions from fission products and environmental sources needs tailor-made ligands for selective recognition and extraction. A ligand group with several phenolate donors [terephthalamide-(dihydroxypyridinone) derivates] was recently reported for the purpose.[45] Earlier it was shown that aminodiphenols are able to transfer uranyl ions from water to dichloromethane.[27] In this process, the length and nature of the alkyl side arm and nature of the substituents in the phenolic moiety significantly influence the extraction efficiency.[27,29] Also, the pH of the system should be as high as possible.[27] In earlier studies,[27] the uranyl ion concentration was 26 mM (6.3 g/L) and the U-to-ligand ratio was 1:4 in a dichloromethane–water two-phase system. TBP extraction was done with 30 vol % ligand in the organic phase and with 10 g/L of U^{VI} ions in water.[15] We have carried out our experiments using 12 mM (2.8 g/L) U^{VI} ion solutions with a (1:1) U-to-L ratio using ammonia as the base in a two-phase system similar to the one used earlier.[27] One reason for using more diluted solutions was the formation of foam during the mixing phase of the extraction. The foam caused problems in the previous experiments,[27] and this was also the case in the present experiments. The use of a more diluted system gives information about the extraction power of the ligands used and also helps the sampling procedure because the foam settles quickly when mixing is stopped during the extraction process.

Extraction of the uranyl ions from water to dichloromethane with H_4L3 was studied at four pH values (2.8, 4.0, 5.0, and 5.7; experiments I). The distribution of the uranyl ions between the phases is presented in Table 3. The actual data are in Tables S1 and S2 in the Supporting Information.

Table 3. Uranium(VI) Distribution after H_4L3 Extraction between Phases at Several pH Values after 6 h

experiment (set I)	pH 2.8	pH 4.0	pH 5.0	pH 5.7
D^a	1.0	1.2	3.4	12
D'^b	1.0	1.2	3.0	12

$^aD = m(U)_o/m(U)_w$, where $m(U)_o$ and $m(U)_w$ are the amounts of uranium in the organic and water phases. $^bD' = m(U)_o/m(U)_b$, where $m(U)_b$ is the amount of uranium in the solid and water phases [$m(U)_b = U_{tot} - m(U)_o$, where U_{tot} is the original mass of uranium].

Clearly, the extraction efficiency in the experiments at pH values of 2.8–5.0 was much lower than that at pH 5.7. This observation is also in line with the previous studies of Schiff base ligands.[45] In the higher-pH experiments, a foam that most likely contains uranyl hydroxide forms between the phases, and therefore the sum of the uranium concentrations in both phases is not 100%, as the samples from both phases reveal. In low pH values (2.8 and 4.0), the formation of foam is minimal, and at pH 5.7, its formation is maximal about 1 h from the beginning of the extraction. It is likely that H_4L3 is capable of reacting also with the foam because the sum of uranium in both phases is nearly 100% at the end of the extraction. From the D' values, it is clear that foam formation is not a problem with H_4L3 in a 6 h extraction.

Next we followed extraction of the uranyl ions from water at pH 5.7 to dichloromethane with H_4L1–H_4L4. The results are presented in Table 4 and in more detail in the Supporting Information (Figure S15 and Tables S3 and S4).

The results show that the highest extraction efficiency $D = 12$ (~92%) was obtained for ligand H_4L3, whereas the lowest $D =$

Table 4. Uranium Distribution between CH_2Cl_2 and Water in Extraction Study II with H_4L1–H_4L4 after 6 h

	H_4L1	H_4L2	H_4L3	H_4L4
D	9.1	10	12	10
D'	1.7	4.9	12	2.4

9.1 (64%, but $D' = 1.7$) was for ligand H_4L1 in a 6 h period. From all of the ligands, H_4L2 and H_4L3 with six and seven CH_2 bridging groups worked more efficiently than the other two, H_4L1 and H_4L4, which also suffer most from the formation of foam. The phenolic Schiff base transfers at pH 5 97% of the uranyl ions to $CHCl_3$.[45] Simple unmodified calixarenes are quite weak uranyl extractors, and they work at quite high pH (8.0).[46]

When the dichloromethane phase extracted with H_4L2 was stored for 2 days at room temperature, compound **5**·$4CH_2Cl_2$ could be isolated; this was verified by X-ray diffraction. This suggests that H_4L2 and H_4L3 can effectively extract uranyl ions as 1:1 complexes, although this may not be the only form extracted. The previous results indicated that two amino-diphenol ligands are needed to extract one uranyl ion.[27] The uranyl ion and ligand can be separated from the complexes using dilute nitric or hydrochloric acid, which makes possible recycling of the ligand.

In a third experiment (III), the uranyl extraction selectivity of the ligands was investigated in the presence of other metal ions because such ions are often present in the processing of fission products. Solutions with equal amounts of metal(II) ions, UO_2^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} ions, as nitrate salts at pH 5.5 were extracted with an equal amount of the ligands (H_4L1–H_4L4, each in a separate experiment) to dichloromethane. The Fe^{III} ion was left out because it easily forms poorly soluble hydroxides at pH 5.5.[47] The results of uranyl ion extractions in the presence of Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} ions with H_4L1–H_4L4 are presented in Tables 5 and S5–S14 in the Supporting Information.

Table 5. Uranium Distribution (D) between CH_2Cl_2 and Water with the Separation Factor ($SF_{U/Cu}$) in Extraction with H_4L1–H_4L4 in a Multimetal System after 4 h

	H_4L1	H_4L2	H_4L3	H_4L4
D	1.4	3.3	2.8	2.4
$SF_{U/Cu}{}^a$	20.7	8.6	7.8	10.1

$^aSF_{U/Cu} = m(U)_o/m(Cu)_o$.

One can conclude that all of these ligands extract the uranyl ion quite well in the presence of Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} ions. Naturally, D values for the uranyl ion extraction are smaller because other metal ions also form complexes with the ligand. Surprisingly, the formation of foam is minimal in this system. The most effective uranyl extractors in this system are H_4L2 ($D = 3.3$) and H_4L3 ($D = 2.8$) at 4 h. The worst extractor is H_4L1 ($D = 1.4$ at 4 h), but it is very selective toward U^{VI} ions because practically none of the other studied transition-metal ions were extracted. With H_4L2–H_4L4, small concentrations of Cu^{II} ions (5–10%) were extracted and also a little of the Co^{II}, Ni^{II}, and Zn^{II} cations (~2% or less; see the Supporting Information). The extraction of Cu^{II} ions with H_4L2–H_4L4 is due to the possible formation of $[Cu_4(Ln)_2(H_2O)_2]$ ($n = 2$–4) because such complexes were formed in the cases of dimethyl derivatives of H_4L3 and H_4L4.[22] Also, aminodiphenols

extracted Cu[II] ions because of the formation of neutral dinuclear units.[28]

This preliminary study shows that these ligands, H4L1–H4L4, are good candidates for selective uranyl extraction. It also reveals that, in general, the extraction capacity is higher with H4L2 and H4L3, which have an alkyl chain of six and seven carbon atoms between the nitrogen donor atoms of the ligands, respectively. Surprisingly, H4L1 extracts most selectively uranyl ions in the presence of Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} ions. The selectivity of H4L1 for uranyl ions is possibly due to the fact that H4L1 does not form neutral extractable complexes with the studied transition-metal ions.

Uranyl extraction was also attempted with nonchlorinated solvents like hexane, toluene, or diethyl ether instead of dichloromethane. The uranyl complexes studied are, in practice, insoluble in these solvents, and the extraction tests were unsuccessful.

CONCLUSIONS

In this work, we have prepared new diaminotetraphenol ligands and studied their coordination chemistry with uranyl ions. We have also used these ligands to extract uranyl ions from water to dichloromethane. Six new uranyl complexes with four diaminotetraphenols (H4L1–H4L4) have been prepared and characterized. All ligands formed 2:1 complexes with uranyl ions, but we were able to isolate solid uranyl complexes in a 1:1 ratio only with the ligands H4L2 and H4L3, although we made several attempts to isolate such complexes with H4L1 and H4L4. The 2:1 complexes are of two types: neutral (**1** and **2**) and anionic (**3** and **4**), with the ligand in a twisted or linear conformation and uranyl ions at both ends of the ligand. In complexes **1**–**4**, uranyl ions have a pentagonal-bipyramidal geometry. In **4**, UO_2^{2+} cations bond simultaneously to nitrate and thiocyanate, which is a rare example of this kind of bonding.

The 1:1 complexes (**5** and **6**) have the formula $[(UO_2)-(H_2Lm)]$ (m = 2 and 3) with cyclic structures, with the uranyl ion in a distorted octahedral geometry. These cyclic neutral complexes crystallize from nonpolar solutions in the presence of solvent molecules of suitable size; these types of uranyl complexes have not been observed before. From the 1:1 complexes, the 2:1 complexes can be prepared by heating in an alcohol solution with uranyl nitrate, as reported in the preparation of compound **2**.

A selective and efficient uranyl extraction method is presented. Uranyl ions transfer from water into a dichloromethane solution possibly best as 1:1 complexes (identified by X-ray diffraction) with ligands H4L2 and H4L3. Also, the 2:1 complexes are soluble in dicloromethane, and in the case of H4L1, uranyl ions also extract as 2:1 complexes but the nature of the complexes formed could not be determined. The alkyl chain length influences the extraction speed (Figure S15 in the Supporting Information). The best extractor was H4L3, which worked fastest, resulting in a 92% extraction in 6 h. In a selectivity test in the presence of Cu[II], Co[II], Ni[II], and Zn[II], 70% extraction was achieved with the H4L3 ligand in 4 h and approximately 90% selectivity was observed. H4L1 is the most selective for uranyl ions in the presence of Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} ions. The uranyl ion can be freed from the complexes using dilute hydrochloric acid, allowing recycling of the ligand (79%).

ASSOCIATED CONTENT

ⓢ Supporting Information

X-ray crystallographic CIF files for complexes **1**–**6**, intermolecular hydrogen bonds in **1** (Figure S1), packing diagrams for **2** and **5** (Figures S2 and S3), NMR and IR spectra of complexes **1**–**6** if they were obtained (Figures S4–S14), details for the uranyl extraction studies (Figure 15 and Tables S1–S14), separation of the uranyl ion from L3[4−]. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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