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Uranyl Complexes with Aroylbis(N,N-dialkylthioureas)

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Supporting Information

ABSTRACT: The reaction of isophthaloylbis(N,N-diethylthiourea), H_2L^1 , with $UO_2(CH_3COO)_2 \cdot 2H_2O$ and NEt₂ as a supporting base gives a tetranuclear, anionic complex of the composition $[{UO_2(L^1)}_4(OAc)_2]^{2-}$, in which the uranyl ions are S,O-chelate bonded. Each two of them are additionally linked by an acetato ligand. Similar reactions of various uranyl starting materials (uranyl acetate, uranyl nitrate, $(NBu_4)_2[UO_2Cl_4]$) with corresponding pyridine-centered ligands (pyridine-2,6dicarbonylbis(N_1N -dialkylthioureas), H_2L^2) yield mononuclear, neutral compounds, in which the thiourea derivatives are coordinated as S,N,N,N,S-five-dentate chelators. The equatorial coordination spheres of the formed hexagonal bipyramidal complexes $[UO_2(L^2)(solv)]$ are completed by solvent ligands



(H₂O, MeOH, or DMF). Attempted reactions without a supporting base result in decomposition of the organic ligands and the formation of hexanuclear uranyl complexes with pyridine-2,6-dicarboxylato ligands, while the use of an excess of base results in condensation and the formation of dinuclear $[{UO_2(L^2)(\mu-OMe)}_2]^{2-}$ complexes. A stable complex of the composition [UO₂(L³)] results from reactions of common uranyl starting materials with 2,2'-bipyridine-6,6'-dicarbonylbis(N,Ndiethylthiourea) (H_2L^3) . The equatorial coordination sphere of the neutral, hexagonal bipyramidal complex is occupied by an SN₄S donor atom set, which is provided by the hexadentate organic ligand. While the uranium complexes with $\{L^1\}^{2-}$ and ${L^2}^{2-}$ are labile and rapidly decompose in acidic solutions, $[UO_2(L^3)]$ is stable over a wide pH range, and the ligand readily extracts uranyl ions from aqueous solutions into organic solvents.

■ INTRODUCTION

During the past three decades, significant progress has been made in the molecular chemistry of the actinides. Typically, the improvement and development of separation techniques for actinide elements in the management and processing of the nuclear fuel cycle is in the focus of interest, but also a deeper insight into their biological distribution patterns with regard to the increasing bioavailability of the elements in mining regions is highly desirable. In recent years, the versatile coordination chemistry particularly of the thorium and uranium has opened a number of new fields of interest. Because uranium is frequently accessible in various oxidation states and has a versatile coordination chemistry, it is also interesting with regard to its general structural chemistry; catalytic, electronic, and magnetic properties of their compounds; and novel reactivity patterns.1-

Although ligand systems combining "hard" and "soft" donor atoms have been proven to increase and control the selectivity of the complexation of metal ions, the coordination chemistry of uranium, particularly that of uranyl compounds, is frequently devoted to ligands with hard donor atoms. The Cambridge Structural Database²¹ contains only one entry of a uranyl compound with a uranium-phosphorus bond²² and less than 60 with U-S bonds, while a larger variety of complexes with soft or mixed hard/soft donor ligands is known for uranium in the oxidation state +4 or +3.²³ This includes, e.g., chalcogenocarbamates,^{24,25} thiosemicarbazones,^{26,27} imidodiphosphinochalcogenides, and bis(thiophosphinoyl)methanediides.²⁸⁻³

Surprisingly, there are no reports about the coordination chemistry of uranium with benzoylthioureas (HL⁰). These versatile ligands form stable complexes with almost all d-block elements and many main group metals.^{36–38} They commonly act as monoanionic *S*,*O* chelators^{39–49} but can also stabilize thiophilic metal ions as neutral S-coordinated ligands.⁵⁰⁻⁵ There are only two technical reports related to uranium. They describe the functionalization of absorbent materials such as activated carbon or resin with benzoylthioureas for the solidphase extraction of uranyl ions.^{53,54} But there is no information about the chemistry involved.

Here, we describe the formation of uranyl complexes with the bipodal aroylthioureas H_2L^1 , H_2L^2 , and H_2L^3 (see Chart 1) as a part of a more comprehensive study about the chemistry of uranium and thorium with such ligands.⁵⁵ Such ligands have been shown to extend the coordination abilities of acylthioureas significantly. Meta-disubstituted, phenyl-centered ligands (e.g., H_2L^1) of this type form binuclear complexes, while

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Chart 1. Aroylthioureas Used Throughout This Paper



trinuclear assemblies are established when the chelating units are in *para*-position to each other.^{56–60} The variation of the central "spacer" (the phenyl ring in H_2L^1) increases the flexibility of the ligand framework and its denticity. Recently, several bimetallic complexes with the pyridine-based ligand H_2L^2 have been described,^{61,62} while a corresponding pyrrole-based ligand does not accommodate metal ions.⁶³ The bipyridine-centered, dianionic ligand { L^3 }^{2–} is potentially hexadentate and tailor-made for the formation of a hexagonal-bipyramidal complex with a { UO_2 }²⁺ unit.⁶⁴

EXPERIMENTAL SECTION

Materials. All chemicals were reagent grade and used without further purification unless otherwise stated. $(NBu_4)_2[UO_2Cl_4]$ was prepared following a standard procedure from uranyl nitrate dissolved in aqueous HCl and $(NBu_4)Cl. H_2L^1$ and H_2L^2 were synthesized according to the literature.^{62,65} THF was distilled from sodium wire and benzophenone, and NEt₃ was distilled over CaH₂. All reactions with air- and moisture-sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques unless otherwise stated.

Physical Measurements. Infrared spectra were taken on a Shimadzu FTIR spectrometer between 400 and 4000 cm⁻¹ from KBr pellets. NMR spectra were recorded at 300 K on a JEOL or ASC64 400 MHz multinuclear spectrometers. ESI mass spectra were measured with an Agilent 6210 ESI-TOF mass spectrometer (Agilent Technologies, Santa Clara, CA, United States). The solvent flow rate was adjusted to 4 μ L/min. The spray voltage was set to 4 kV, and the drying gas flow rate to 15 psi (1 bar). All other parameters were adjusted for a maximum abundance of the relative $[M + H]^+$ or [M]ions. Calibration salts are the source for the alkaline ions of the Na⁺ and K⁺ cluster ion peaks. All MS results are given in the form: m/z_1 assignment. Because of radiation safety, not all the radioactive compounds were measured. For a series of complexes, some representatives were selected. Elemental analyses of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus Vario EL elemental analyzer. UV/vis spectra were recorded on a SPECORD 40 instrument (Analytik Jena). The uranium contents of the samples were measured by a HIDEX 300 SL liquid scintillation counter. An aliquot (0.2 mL) of each sample was added to 10 mL of a scintillation cocktail (Rotiszint ecoplus, Carl Roth), and the net count rates were measured over 1024 channels with a counting time of 120 s.

Health Precautions. All work with radioactive material was done in a well-ventilated cupboard in a lab approved for the handling of uranium compounds.

Synthesis of H₂L³. 6,6'-Dicyano-2,2'-bipyridine. The compound was synthesized according to the method outlined by Sharmoukh and Allam with some modifications.⁶⁶ A solution of benzoyl chloride (24 mL, 208 mmol) in 80 mL of dichloromethane was added dropwise

during approximately 30 min to a cold mixture of 2,2'-bipyridine-N,N'-dioxide (11.2 g, 60 mmol) and potassium cyanide (22.5 g, 345 mmol) in 200 mL of deionized water. The reaction mixture was stirred for 4 h, and the obtained precipitate was filtered off, thoroughly washed with ethanol, and dried in vacuum. Yield: 70% (8.8 g). Elemental analysis: Calcd for C₁₂H₆N₄: C, 69.90; H, 2.93; N 27.17%. Found: C, 69.97; H, 2.80; N, 27.23%. IR (KBr, cm⁻¹): 3080 (w), 2972(w), 2929(w), 2236 (m), 2010(w), 1576 (s), 1433 (s), 1209 (w), 1156 (s), 1080 (m), 989 (s), 801 (s), 734 (m). ¹H NMR ((CD₃)₂SO, ppm): 8.03–7.98 (m, 2H, bipy); 7.78 (t, 2H, *J* = 7.2 Hz, bipy); 7.52–7.43 (m, 2H, bipy). ¹³C NMR ((CD₃)₂SO, ppm): 154.9 (C=N); 138.7, 131.9, 128.9, 124.2, 116.6 (bipy).

2,2'-Bipyridine-6,6'-dicarboxylic Acid. 6,6'-Dicyano-2,2'-bipyridine (5.5 g, 26.5 mmol) was added to a solution of NaOH (9.5 g, 238.3 mmol) in H₂O/EtOH (100 mL/100 mL) and stirred at 80 °C for 3 days. After cooling, the reaction mixture was neutralized with conc HCl. The obtained precipitate was filtered off and washed thoroughly with EtOH. A pure product was obtained after recrystallization from EtOH/H₂O. Yield: 80% (5.1 g). Elemental analysis: Calcd for C₁₂H₈N₂O₄: C, 59.02 H, 3.30; N, 11.47%. Found: C, 58.84; H, 3.36; N, 11.00%. IR (KBr, cm⁻¹): 3095(w), 2982(w), 2838(w), 2555(w), 1692(vs), 1583(s), 1452(m), 1398(s), 1313(s), 1265(m), 1172(w), 1080(m), 938(m), 824(m), 762(vs), 692(s). ¹H NMR ((CD₃)₂SO, ppm): 8.74 (d, 2H, J = 7.2 Hz, bipy); 8.19–8.13 (m, 4H, bipy). ¹³C NMR ((CD₃)₂SO, ppm): 165.9 (C=O); 154.4, 148.1, 139.0, 125.3, 124.2 (bipy).

2,2'-Bipyridine-6,6'-dicarbonyl Dichloride. 2,2'-Bipyridine-6,6'dicarboxylic acid (5 g, 20.5 mmol) was mixed with an excess of SOCl₂ (25 mL) and 2 drops of DMF and heated on reflux for 6 h. The solvent was then removed under reduced pressure, and the resulting colorless solid was dried under vacuum. Yield: 99% (5.7 g). IR (KBr, cm⁻¹): 3085 (w), 2972(w), 2929(w), 1748 (vs), 1575 (w), 1439 (w), 1242 (s), 1157 (m), 954 (m), 864 (s), 733 (s), 623 (s). ¹H NMR (CDCl₃, ppm): 8.98 (dd, 2H, J_1 = 1.1 Hz, J_2 = 7.8 Hz, bipy); 8.18 (dd, 2H, J_1 = 1.1 Hz, J_2 = 7.8 Hz, bipy); 8.10 (t, 2H, J = 8.0 Hz, bipy). ¹³C NMR (CDCl₃, ppm): 169.7 (C=O); 154.4, 149.3, 139.4, 125.3, 124.2 (bipy).

 H_2L^3 . A solution of N,N-diethylthiourea (Et₂tu) (5.2 g, 40 mmol) in 100 mL of dry THF was added dropwise to a solution of 2,2'bipyridine-6,6'-dicarbonyl dichloride (5.6 g, 20 mmol) in 100 mL of dry THF at room temperature. After being stirred for 1 h, dry triethylamine (4.2 mL, 30 mmol) was added, and the reaction mixture was stirred at 50 °C for an additional 45 min. The formed colorless precipitate (HNEt₃Cl) was filtered off, and the remaining solvent was removed under reduced pressure. The yellow product was recrystallized from methanol/chloroform (5:1). Yield: 65% (6.3 g). Elemental analysis: Calcd for C₂₂H₂₈N₆O₂S₂: C, 55.91; H, 5.97; N, 17.78; S, 13.57%. Found: C, 55.92; H, 5.97; N, 17.72; S, 13.59%. IR (KBr, cm⁻¹): 3375(m), 3318(m), 3190(m), 3082(w), 2972(m), 2929(w), 1707(vs), 1627(m), 1581(m), 1521(s), 1467(w), 1419(s), 1363(m), 1280(m), 1219(m), 1126(m), 1074(m), 1014(w), 931(w), 861(w), 756(m), 667(w). ¹H NMR (CDCl₃, ppm): 10.21 (s, 2H, NH); 8.54 (dd, 2H, $J_1 = 1.2$ Hz, $J_2 = 8.0$ Hz, bipy); 8.26 (dd, 2H, $J_1 = 1.1$ Hz, $J_2 = 8.0$ Hz, bipy); 8.08 (t, 2H, J = 8.0 Hz, bipy): 4.06–4.04 (m, 4H, CH₂); 3.71–3.68 (m, 4H, CH₂); 1.37–1.20 (m, 12H, CH₃). ¹³C NMR (CDCl₃, ppm): 178.6 (C=S); 159.8 (C=O); 153.8, 148.1, 139.1, 124.7, 123.9 (bipy); 47.9, 45.6, (CH₂); 13.5, 12.5 (CH₃). ESI+MS (m/z): 511.1364 (calcd. 511.1352) [M+K]⁺; 495.1625 (calcd. 495.1613) [M + Na]⁺; 473.1806 (calcd. 473.1793) [M + H]⁺. UV/vis (CH₂Cl₂, nm): 218 ($\varepsilon = 43.6 \times 10^3$ L mol⁻¹cm⁻¹), 246 ($\varepsilon = 59.5 \times 10^3$ L mol⁻¹cm⁻¹).

Syntheses of the Complexes. $(NBu_4)_2[{UO_2(L^1)}_4(OEt)_2(HOEt)_2]$. H₂L¹ (39.4 mg, 0.1 mmol) was dissolved in EtOH (3 mL) and added to a stirred solution of (NBu₄)₂[UO₂Cl₄] (90 mg, 0.1 mmol) in EtOH (3 mL). After 10 min, 3 drops of NEt₃ were added, and the reaction mixture was stirred at room temperature for 1 h. The orange-red precipitate was collected by filtration, washed with EtOH, and dried in vacuum. Single crystals for X-ray diffraction were obtained after slow evaporation of a CH₂Cl₂/EtOH 1:1 (v/v) solution at room temperature. Yield: 40% (33 mg). Elemental analysis: Calcd for C112H190N18O20S8U4: C, 40.55; H, 5.77; N, 7.60; S, 7.73%. Found: C, 40.54; H, 5.59 N, 7.88; S, 8.25%. IR (KBr, cm⁻¹): 3446 (m), 2966 (m), 2931 (m), 2873 (w), 1595 (w), 1500 (vs), 1423 (s), 1394 (s), 1309 (w), 1251 (w), 1140 (m), 1078 (m), 910 (s), 825 (m), 729 (m), 669 (w). ¹H NMR (CD₂Cl₂, ppm): 11.30 (s, 2H, OH_EtOH); 8.43 (m, 4H, Ph), 8.34 (d, 8H, I = 7.6 Hz, Ph), 7.49 (m, 4H, Ph); 4.26-4.05 (m, 32H, CH₂); 2.55-2.41 (m, 24H, CH₂ NBu₄, CH₂ EtOH), 1.48-1.24 (m, 32H, CH₂NBu₄); 1.01-0.92 (m, 48H, CH₃); 0.82 (t, 12H, J = 7.1 Hz, CH₃_EtOH); 0.65–0.61 (m, 18H, CH₃ NBu₄). ¹³C NMR (CD₂Cl₂, ppm): 184.2 (C=S); 173.3 (C=O); 137.2, 132.9, 131.1, 127.6 (Ph); 57.8 (CH₂ EtOH); 47.6, 46.3 (CH₂); 45.9 (CH₂_NBu₄); 23.2 (CH₂_NBu₄); 19.2 (CH₂_NBu₄); 13.2 (CH₃_EtOH); 13.4, 12.3 (CH₃); 8.9 (CH₃_NBu₄). UV/vis (CH_2Cl_2, nm) : 232 ($\varepsilon = 12.5 \times 10^3 \text{ L mol}^{-1}\text{cm}^{-1}$), 283 ($\varepsilon = 11.5$ $\times 10^{3}$ L mol⁻¹cm⁻¹), 368 ($\varepsilon = 1.8 \times 10^{3}$ L mol⁻¹cm⁻¹).

 $(HNEt_3)_2[{UO_2(L^1)}_4(OAc)_2]$. H_2L^1 (39.4 mg, 0.1 mmol) was dissolved in EtOH (3 mL) and added to a stirred solution of UO₂(CH₃COO)₂·2H₂O (42.4 mg, 0.1 mmol) in EtOH (3 mL). After 10 min, 3 drops of NEt₃ were added, and the reaction mixture was stirred at room temperature for 1 h. The orange-red precipitate was collected by filtration, washed with MeOH, and dried in vacuum. Single crystals for X-ray diffraction were obtained after slow evaporation of a CH₂Cl₂/MeOH 1:1 (v/v) solution at room temperature. Yield: 68% (52 mg). Elemental analysis: Calcd for $C_{90}H_{138}Cl_4N_{18}O_{20}S_8U_4$ ((HNEt₃)₂[{UO₂(L¹)}₄(OAc)₂]·2CH₂Cl₂): C, 34.40; H, 4.43; N, 8.02; S, 8.16%. Found: C, 34.42; H, 4.40; N, 8.01; S, 8.27%. IR (KBr, cm⁻¹): 3062(w), 2976 (w), 2931 (w), 2872 (w), 1680 (w), 1587 (w), 1500 (vs), 1426 (s), 1382 (s), 1311 (w), 1251 (w), 1138 (m), 1078 (m), 1010 (w), 910 (s), 827 (m), 729 (m), 653 (w). ¹H NMR (CDCl₃, ppm): 10.23 (s, 4H, Ph), 8.44 (dd, 8H, J₁ = 8.0 Hz, J_2 = 2.0 Hz, Ph), 7.46 (t, 4H, J = 8.0 Hz, Ph); 4.35-3.74 (m, 32H, CH₂); 3.00 (s, 6H, CH₃OAc); 2.26 (m, 6H, CH₂_HNEt₃), 1.37–1.08 (m, 48H, CH₃); 0.63 (t, 18H, J = 7.7 Hz, CH₃_HNEt₃). ¹³C NMR (CDCl₃, ppm): 184.8 (C=S); 173.1 (C= O OAc); 170.4 (C=O); 137.2, 132.8, 131.6, 127.8 (Ph); 47.7, 46.1 (CH₂); 45.6 (CH₂_HNEt₃); 25.6 (CH₃_OAc); 13.6, 12.6 (CH₃); 8.4 $(CH_3 HNEt_3)$. UV/vis (CH_2Cl_2, nm) : 232 ($\varepsilon = 12.5 \times 10^3 L mol^{-1}cm^{-1}$), 283 ($\varepsilon = 11.5 \times 10^3 L mol^{-1}cm^{-1}$), 368 ($\varepsilon = 1.8 \times 10^3 L$ $mol^{-1}cm^{-1}$).

 $[UO_2(dipicolinate)(H_2O)]_6$. H_2L^{2a} (39.5 mg, 0.1 mmol) was dissolved in MeOH (3 mL) and added to a stirred solution of $(NBu_4)_2[UO_2Cl_4]$ (90 mg, 0.1 mmol) or $UO_2(CH_3COO)_2\cdot 2H_2O$ (42.4 mg, 0.1 mmol) or $UO_2(NO_3)_2\cdot 6H_2O$ (50.2 mg, 0.1 mmol) in MeOH (3 mL), and the reaction mixture was stirred for 1 h. Single crystals for X-ray diffraction were obtained after slow evaporation of the mother solution at room temperature. Yield: 60% (27 mg). IR (KBr, cm⁻¹): 3267(s), 3070(w), 2972(m), 2934(m), 2874(w), 1628(vs), 1522(vs), 1470(vs), 1445(vs), 1417(vs), 1377(m), 1343(w), 1274(m), 1225(s), 1169(m), 1130(m), 1101(m),

998(m), 943(m), 922(s), 862(s), 764(s), 682(m). UV/vis (CH₂Cl₂, nm): 230 (ε = 3.2 × 10³ L mol⁻¹cm⁻¹), 260 (ε = 4.4 × 10³ L mol⁻¹ cm⁻¹), 368 (ε = 0.4 × 10³ L mol⁻¹ cm⁻¹).

 $[UO_2(L^{2a})(MeOH)]$. H₂L^{2a} (39.5 mg, 0.1 mmol) was dissolved in MeOH (3 mL) and added to a stirred solution of $(NBu_4)_2[UO_2Cl_4]$ (90 mg, 0.1 mmol) or $UO_2(CH_3COO)_2 \cdot 2H_2O$ (42.4 mg, 0.1 mmol) in MeOH (3 mL). Two drops of NEt₃ were added, and the reaction mixture was stirred for 1 h. Single crystals for X-ray diffraction were obtained after slow evaporation of the mother solution at room temperature. Yield: 70% (48 mg). Elemental analysis: Calcd for C₁₈H₂₇N₅O₅S₂U: C, 31.08; H, 3.91; N, 10.07; S, 9.22%. Found: C, 31.09; H, 3.90; N, 10.05; S, 9.21%. IR (KBr, cm⁻¹): 3211(w), 2972(w), 2935(w), 2873(w), 1654(vs), 1591(s), 1523(s), 1429(s), 1396(s), 1348(m), 1313(w), 1263(m), 1205(w), 1151(m), 1078(m), 1016(m), 945(m), 912 (vs), 850(m), 763(m), 680(w). ¹H NMR $((CD_3)_2SO, ppm): 8.51 (d, 2H, J = 8.4 Hz, py); 8.43 (t, 1H, J = 8.4$ Hz, py); 3.97-3.91 (m, 4H, CH₂); 3.55-3.50 (m, 4H, CH₂); 1.24 (t, 6H, J = 7.0 Hz, CH₃); 1.01 (t, 6H, J = 7.0 Hz, CH₃). ¹³C NMR ((CD₃)₂SO, ppm): 191.3 (C=S); 174.8 (C=O); 142.4, 139.6, 125.9 (py); 45.1, 46.1 (CH₂); 12.3, 13.5 (CH₃). ESI+ MS (m/z): 1365.3036 (calcd. 1365.3036) [{2M-MeOH}+K]⁺; 702.1331 (calcd. 702.1336) [{M-MeOH}+K]⁺. UV/vis (CH₂Cl₂, nm): 232 $(\varepsilon = 4.1 \times 10^3 \text{ L mol}^{-1}\text{cm}^{-1}), 281 \ (\varepsilon = 3.3 \times 10^3 \text{ L mol}^{-1}\text{cm}^{-1}), 397 \ (\varepsilon = 0.4 \times 10^3 \text{ L mol}^{-1}\text{cm}^{-1}).$

 $[UO_2(L^{2a})(DMF)]$. Yellow needles of the compound were synthesized by dissolving [UO₂(L^{2a})(MeOH)] (35 mg, 0.05 mmol) in DMF (1 mL) and slow evaporation of the solvent at room temperature. Yield: 90% (36 mg). Elemental analysis: Calcd for C₂₃H₃₇N₇O₆S₂U $([UO_2(L^{2a})(DMF)] \cdot DMF)$: C, 34.12 H, 4.61; N, 12.11; S, 7.92%. Found: C, 34.11; H, 4.61; N, 12.10; S, 7.89%. IR (KBr, cm⁻¹): 3429(w), 2972(w), 2933(w), 2872(w), 1668(w), 1629(vs), 1593(w), 1517(m), 1429(m), 1373(s), 1317(w), 1286(w), 1259(m), 1205(w), 1149(m), 1091(m), 1014(m), 948(m), 904(vs), 842(m), 761(m), 677(w), 653(w), 638(w). ¹H NMR ((CD₃)₂SO, ppm): 8.48 (d, 2H, J = 8.0 Hz, py); 8.40 (t, 1H, J = 8.0 Hz, py); 7.86 (s, 2H, CH_DMF); 3.97-3.91 (m, 4H, CH₂); 3.55-3.49 (m, 4H, CH₂); 2.83 (s, 12H, CH₃ DMF); 1.23 (t, 6H, J = 7.0 Hz, CH₃); 1.00 (t, 6H, J = 7.0 Hz, CH_3). ¹³C NMR ((CD₃)₂SO, ppm): 191.4 (C=S); 163.2 (C= O DMF); 158.4 (C=O); 121.5, 125.9, 142.4 (py); 45.1, 46.1, (CH₂); 31.3, 36.3 (CH₃ DMF); 12.2, 13.4 (CH₃). ESI+ MS (*m*/*z*): 2012.4997 (calcd. 2012.4996) [3{M-DMF}+Na]; 1349.3322 (calcd. 1349.3296) [2{M-DMF}+Na]; 686.1625 (calcd. 686.1597) [{M-DMF}+Na].

 $[UO_{2}(L^{2b})(OH_{2})]$. H₂L^{2b} (42.3 mg, 0.1 mmol) was dissolved in MeOH (3 mL) and added to a stirred solution of (NBu₄)₂[UO₂Cl₄] (90 mg, 0.1 mmol) or UO₂(CH₃COO)₂·2H₂O (42.4 mg, 0.1 mmol) in MeOH (3 mL). After 10 min, 2 drops of NEt₃ were added and the reaction mixture was stirred for 1 h. The light-yellow precipitate was collected by filtration, washed with MeOH, and dried in vacuum. Single crystals for X-ray diffraction were obtained after slow evaporation of a CH₂Cl₂/MeOH 1:1 (v/v) solution at room temperature. Yield: 60% (42 mg). Elemental analysis: Calcd for C17H21N5O7S2U: C, 28.78; H, 2.98; N, 9.87; S, 9.04%. Found: C, 28.78 H, 2.98; N, 9.89; S, 9.04%. IR (KBr, cm⁻¹): 3229(m), 2972(w), 2920(w), 2854(w), 1606(vs), 1516(s),1429(m), 1386(s), 1298(m), 1236(w), 1105(m), 1024(m), 912 (vs), 846(m), 766(w), 698(w), 551(w). ¹H NMR ((CD₃)₂SO, ppm): 8.50 (d, 2H, J = 6.8 Hz, py); 8.44 (t, 1H, J = 6.8 Hz, py); 3.81–3.51 (m, 16H, CH₂). ¹³C NMR ((CD₃)₂SO, ppm): 192.1 (C = S); 162.8 (C=O); 158.2, 142.4, 126.1 (py); 66.4 (CH₂-O); 46.2 (CH₂-N). ESI+ MS (m/z): 2096.3828 (calcd. 2096.3751) $[{M-H_2O}_3+Na]^+$; 1405.2538 (calcd. 1405.2467) [2{M-H₂O}+Na]⁺; 730.0963 (calcd. 730.0922) [{M-H₂O}+K]⁺; 714.1232 (calcd. 714.1182) [{M-H₂O}+Na]⁺. UV/vis $(CH_2Cl_2, nm): 230 \ (\varepsilon = 3.4 \times 10^3 \text{ L mol}^{-1}\text{ cm}^{-1}), 269 \ (\varepsilon = 2.6 \times 10^3 \text{ L mol}^{-1}\text{ cm}^{-1}), 370 \ (\varepsilon = 0.4 \times 10^3 \text{ L mol}^{-1}\text{ cm}^{-1}).$

 $[UO_2(L^{2b})(DMF)]$. The compound was synthesized by dissolving $[UO_2(L^{2b})(OH_2)]$ (35 mg, 0.05 mmol) in DMF (1 mL) and slow evaporation of the solvent at room temperature. Yield: 92% (35 mg). Elemental analysis: Calcd for $C_{20}H_{26}N_6O_7S_2U$: C, 31.42; H, 3.43; N, 10.99; S, 8.39%. Found: C, 31.40; H, 3.44; N, 10.99; S, 8.37%. IR

(KBr, cm⁻¹): 3446(w), 2960(w), 2924(w), 2856(w), 1631(s), 1595(w), 1500(vs),1423(m), 1371(s), 1298(m), 1232(w), 1111(m), 1066(w), 1033(m), 908 (vs), 844(m), 759(w), 677(w), 634(w), 607(w), 553(w), 505(w). ¹H NMR ((CD₃)₂SO, ppm): 8.50 (d, *J* = 7.0 Hz, 2H, py), 8.45 (t, *J* = 7.0 Hz, 1H, py), 7.86 (s, 1H, CH_DMF), 3.88–3.55 (m, 16H, CH₂), 2.86 (s, 6H, CH₃_DMF). ¹³C NMR ((CD₃)₂SO, ppm): 192.1 (C=S), 164.5 (C=O_DMF), 159.7 (C=O), 148.6, 133.2, 126.1 (py), 66.7 (CH₂–O), 46.2 (CH₂–N), 36.3, 31.5 (CH₃_DMF). ESI+ MS (*m*/*z*): 1405.2505 (calcd. 1405.2467) [{M-DMF}₂+Na]⁺; 730.1010 (calcd. 730.0922) [{M-DMF+K]⁺; 714.1219 (calcd. 714.1182) [{M-DMF}+Na]⁺; 692.1401 (calcd. 692.1363) [{M-DMF+H]⁺.

 $(HNEt_3)_2[{UO_2(L^{2a})(\mu^2-OMe)}_2]$. (a) $[UO_2(L^{2a})(MeOH)]$ (69.5 mg, 0.1 mmol) was dissolved in 5 mL of warm methanol and NEt₃ (2 drops) was added. Orange-yellow crystals precipitated after cooling and partial evaporation of the solvent. Yield: 80% (64 mg). (b) H_2L^{2a} (19.8 mg, 0.05 mmol) was dissolved in MeOH (3 mL) and added to a stirred solution of $(NBu_4)_2[UO_2Cl_4]$ (90 mg, 0.1 mmol) or $UO_2(CH_3COO)_2 \cdot 2H_2O$ (42.4 mg, 0.1 mmol) in MeOH (3 mL). Two drops of NEt₃ were added, and the reaction mixture was stirred for 1 h. The obtained precipitate was filtered off, washed with MeOH, and dried under vacuum. Single crystals for X-ray diffraction were obtained after slow evaporation of a $CH_2Cl_2/MeOH$ 1:2 (v/v) solution at room temperature. Yield: 74% (59 mg).

Elemental analysis: Calcd for $C_{48}H_{84}N_{12}O_{10}S_4U_2$: C, 35.76; H, 5.17; N, 10.65; S, 8.12%. Found: C, 35.55; H, 5.27; N, 10.41; S, 8.10%. IR (KBr, cm⁻¹): 3429(m), 3070(w), 2974(m), 2933(w), 2874(w), 2681(w), 1589 (vs), 1497(m), 1462(w), 1425(m), 1382(s), 1309(m), 1278(m), 1247(s), 1201(w), 1145(m), 1120(m), 1070(m), 1016(m), 950(w), 912 (vs), 868(w), 766(s), 678(w), 638(m). UV/ vis (CH₂Cl₂, nm): 230 (ε = 8.3 × 10³ L mol⁻¹cm⁻¹), 265 (ε = 7.8 × 10³ L mol⁻¹cm⁻¹), 304 (ε = 4.9 × 10³ L mol⁻¹cm⁻¹), 368 (ε = 1.2 × 10³ L mol⁻¹cm⁻¹).

(*HNEt*₃)₂[{ $UO_2(L^{2b})(\mu^2-OMe)$ }₂]. (a) [$UO_2(L^{2a})(OH)_2$] (71, mg, 0.1 mmol) was dissolved in 5 mL of warm methanol and NEt₃ (2 drops) was added. Yellow crystals deposited after cooling and partial evaporation of the solvent. Yield: 71 mg (58 mg). (b) H_2L^{2b} (84.6 mg, 0.2 mmol) was dissolved in MeOH (3 mL) and added to a stirred solution of $(NBu_4)_2[UO_2Cl_4]$ (90 mg, 0.1 mmol) or $UO_2(CH_3COO)_2$ ·2H₂O (42.4 mg, 0.1 mmol) in MeOH (3 mL). Two drops of NEt₃ were added, and the reaction mixture was stirred for 1 h. The obtained precipitate was filtered off, washed with MeOH, and dried under vacuum. Single crystals for X-ray diffraction were obtained after slow evaporation of a $CH_2Cl_2/MeOH$ 1:1 (v/v) solution at room temperature. Yield: 77% (76 mg).

Elemental analysis: Calcd for $C_{48}H_{76}N_{12}O_{14}\tilde{S}_4U_2$: C, 34.95; H, 4.64; N, 10.19; S, 7.77%. Found: C, 35.17; H, 5.09; N, 9.53; S, 7.62%. IR (KBr, cm⁻¹): 3428(w), 2976(w), 2922(w), 2855(w), 2683(w), 1587(vs), 1475(m), 1427(s), 1381(m), 1280(s), 1229(m), 1111(m), 1064(w), 1026(m), 951(m), 901 (s), 841(m), 777(m), 760(m), 702(w), 629(m). UV/vis (CH₂Cl₂, nm): 230 (ε = 3.4 × 10³ L mol⁻¹cm⁻¹), 269 (ε = 2.6 × 10³ L mol⁻¹cm⁻¹), 370 (ε = 0.4 × 10³ L mol⁻¹cm⁻¹).

 $[UO_2(L^3)]$. H₂L³ (42.3 mg, 0.1 mmol) was dissolved in MeOH (3 mL) and added to a stirred solution of (NBu₄)₂[UO₂Cl₄] (90 mg, 0.1 mmol) or UO₂(CH₃COO)₂·2H₂O (42.4 mg, 0.1 mmol) in MeOH (3 mL). Two drops of NEt₃ were added, and the reaction mixture was stirred for 1 h. The light-yellow precipitate was collected by filtration, washed with MeOH, and dried under vacuum. Single crystals for Xray diffraction were obtained after slow evaporation of a CH2Cl2/ MeOH 1:1 (v/v) solution at room temperature. Yield: 90% (67 mg). Elemental analysis: Calcd for C₂₂H₂₆N₆O₄S₂U: C, 35.68; H, 3.54; N, 11.35 S, 8.66%. Found: C, 35.67; H, 3.61; N, 11.36; S, 8.63%. IR $(KBr, cm^{-1}): 2972(w), 2937(w), 2873(w), 1637(vs), 1598(m),$ 1517(vs), 1458(m), 1409(m), 1371(s), 1330(w), 1284(w), 1244(m), 1149(m), 1087(m), 1014(m), 908(vs), 819(m), 761(m), 671(w). ¹H NMR ((CD₃)₂SO, ppm): 9.13 (d, 2H, J = 8.0 Hz, bipy), 8.68 (t, 1H, J = 8.0 Hz, bipy), 8.61 (d, 2H, J = 8.0 Hz, bipy), 4.13–4.08 (m, 4H, CH₂), 3.84–3.79 (m, 4H, CH₂), 1.40–1.36 (t, 6H, J = 7.3 Hz, CH₃), 1.23-1.19 (t, 6H, J = 7.3 Hz, CH₃). ¹³C NMR ((CD₃)₂SO, ppm):

182.0 (C=S), 161.6 (C=O), 156.8, 155.9, 143.2, 127.3, 127.0 (bipy), 47.1, 46.1, (CH₂), 12.9, 12.8 (CH₃). ESI+ MS (m/z): 779.1550 (calcd. 779.1602) [M+K]⁺; 763.1816 (calcd. 763.1862) [M + Na]⁺; 741.1991 (calcd. 741.2043) [M + H]⁺. UV/vis (CH₂Cl₂, nm): 230 (ε = 2.4 × 10³ L mol⁻¹cm⁻¹), 260 (ε = 2.2 × 10³ L mol⁻¹cm⁻¹).

Stability Tests. The complexes (HNEt₃)₂[{UO₂(L¹)}₄(OAc)₂], [UO₂(L^{2a})(MeOH)], [UO₂(L^{2b})(H₂O)], and [UO₂(L³)] were used for the two-phase extraction experiments. They were performed at room temperature in microcentrifuge tubes (5 mL) with a phase ratio $V_{(org)}:V_{(aq)}$ of 2:2 mL. The pH of the aqueous phase was adjusted with nitric acid, and a constant ionic strength was maintained by the addition of (NEt₄)NO₃ (0.5 mM). The organic phase (0.4 mM) was prepared by dissolving the complexes in CH₂Cl₂. The samples were shaken for 30 min. The aqueous phase was separated from the organic one, and the depletion of the uranyl ions was monitored in suitable aliquots (usually 200 μ L), measuring the concentration of the uranyl ions radiometrically using a liquid scintillation counter. The remaining organic phase was analyzed by UV/vis spectroscopy.

Computational Details. DFT (density functional theory) calculations were performed with the high-performance computing system of the ZEDAT (SOROBAN)⁶⁷ using the program packages GAUSSIAN 09 and GAUSSIAN 16.^{68,69} The gas phase geometry optimizations were performed using coordinates derived from the X-ray crystal structures or by modification of the structures using GAUSSVIEW. The calculations for the ligand molecules H_2L^1 , H_2L^{2a} , and H_2L^{2b} were performed without any restrictions on the structures by using the hybrid density functional B3LYP together with the standard basis set 6-311G for all atoms.^{70–72} For molecules containing uranium, the calculations were also performed without any restrictions on the structures by using the hybrid density functional B3LYP,^{70–72} together with the basis sets obtained from the EMSL database 6-311++G for all atoms excluding uranium. For uranium, the pseudopotential LANL2DZ was used.^{73,74}

X-ray Crystallography. The intensities for the X-ray determinations were collected on STOE IPDS 2T or Bruker D8 Venture instruments with Mo K α or Cu K α radiation. The space groups were determined by the detection of systematical absences. Absorption corrections were carried out by SADABS or X-RED32.75-⁷⁷ Structure solutions were performed with the programs SHELXS 86, SHELXS 97, and SHELXS 2014; structure refinements were done with the SHELXL 2014 program.^{78,79} Hydrogen atoms were placed at calculated positions and treated with the "riding model" option of SHELXL. For $[UO_2(L^{2a})(MeOH)]$ and $[UO_2L^{2b}(H_2O)]$, the hydrogen atoms of the solvent molecules (methanol and water) were located on the basis of the electron density of the Fourier map and refined. Details about the measurement and refinement data are summarized in the Supporting Information. The structures of the representation of molecular structures was done using the programs DIAMOND 4.2.2.80 Because ball and stick presentations of the molecules are used in most of the figures of this paper for reasons of clarity, ellipsoid representations of all compounds are contained in the Supporting Information.

The structure measurements of $(NBu_4)_2[\{UO_2(L^1)\}_4(OEt)_2(HOEt)_2 \text{ are not of sufficient quality to justify a detailed discussion of bond lengths and angles or the deposit in the crystallographic database. For this reason, they are not included in the crystallographic material. But, they doubtlessly confirm the structures of the compounds and are used as such in the following discussion. Additional information on the structure determinations is contained in the Supporting Information and has been deposited with the Cambridge Crystallographic Data Centre.$

RESULTS AND DISCUSSION

The synthesis of the bipodal isophthaloylbis(N,N-diethylthiourea), H_2L^1 , was done in a one-pot reaction from isophtaloyl chloride, (NH_4)SCN, and diethylamine as has been reported by Koch et al.⁵⁶ Such an approach works perfectly for the phenyl-centered ligand but cannot be applied

Scheme 1. Synthesis of H_2L^2







Figure 1. Molecular structure of H_2L^3 .

for the ligands H_2L^2 and H_2L^3 , which possess pyridine functionalities. They require a presynthesis of *N*,*N*-dialkylthioureas,⁸¹ which can then be coupled to the appropriate carboxylic acid chloride (Scheme 1).⁶² The use of THF instead of acetone as solvent for such reactions improves the yields to up to 90% because H_2L^{2a} and H_2L^{2b} are slightly soluble in acetone. The morpholine-derivative H_2L^{2b} was added to this work because the additional oxygen donor atoms may generate interesting inter- or intramolecular interactions, as has been shown in a previous work.⁶¹

For the synthesis of 2,2'-bipyridine-6,6'-dicarbonylbis(N,Ndiethylthiourea), the dichloride of 2,2'-bipyridine-6,6'-dicarboxylic acid was synthesized prior to the coupling reaction with Et₂tu (N,N-diethythiourea) as is shown in Scheme 2. First, 2,2bipyridine is converted into 2,2'-bipyridine-N,N'-dioxide, followed by its functionalization with a cyanide groups. The resulting 6,6'-dicyano-2,2'-bipyridine is then hydrolyzed, and the dicarboxylic acid is obtained as a colorless precipitate with a final yield of about 50%. It is converted into the corresponding dichloride by heating with an excess of thionyl chloride. H_2L^3 is obtained from the reaction of the dichloride with two equivalents of Et₂tu in the presence of triethylamine. The colorless product is soluble in solvents such as THF, acetone, CH₂Cl₂, or CHCl₃. The IR spectrum of H₂L³ shows a band at 3375 cm⁻¹, which corresponds to the N-H stretch. The strong absorption band at 1707 cm⁻¹ can be assigned to the C=O vibration. The ¹H NMR spectrum in $CDCl_3$ is characterized by a singlet at 10.21 ppm belonging to the N-H

protons. The resonances of the aromatic protons are observed at 8.56, 8.26, and 8.08 ppm. The hindered rotation around the C(S)-NEt₂ bond, which is found in many benzoylthioureas,⁴⁹ is also observed in H₂L³. This results in a magnetic inequivalence of the two diethyl residues. Two multiplets at 4.04 and 3.68 ppm for the CH₂ protons and one multiplet at 1.20 ppm for the CH₃ protons are observed. The composition of the ligand is also confirmed by its ESI+ mass spectrum with the molecular ion $[M + H]^+$ peak at m/z = 473.1806.

Single crystals of H_2L^3 were obtained after recrystallization from a $CH_2Cl_2/diethyl$ ether (1:5) mixture. Figure 1 shows the molecular structure of the compound. Only half of the molecule is contained in the asymmetric unit. The complete ligand is produced by an inversion center being located between C25 and C25'. The C–O bond length of 1.214(2) Å and the C–S bond length of 1.673(2) Å are within the expected ranges of corresponding double bonds. The C2–N3 and C4–N3 bond lengths are 1.406(2) and 1.380(2) Å, respectively, and reflect a partial double bond character, suggesting a delocalization of π -electron density. Similarities with these observed values were previously reported for other bipodal aroylthioureas.^{63,82} More bond lengths and angles are given in the Supporting Information.

The three bipodal thiourea ligands H_2L^1 , H_2L^2 and H_2L^3 were reacted with common uranyl starting materials such as $UO_2(CH_3COO)_2 \cdot 2H_2O$ or $(NBu_4)_2[UO_2Cl_4]$. In some cases (particularly when the acidic $(NBu_4)_2[UO_2Cl_4]$ was used), the addition of NEt₃ as a supporting base was required to



Scheme 3. Reactions of Uranyl Salts with the Bipodal Aroylthioureas under Study and Their Products

Figure 2. Structure of the $[{UO_2(L^1)}_4(OAc)_2]^{2-}$ anion.

deprotonate the organic ligands and avoid decomposition of the ligands. A summary of the performed reactions and the obtained products is given in Scheme 3.

Treatment of $UO_2(CH_3COO)_2 \cdot 2H_2O$ with an equivalent amount of H₂L¹ in EtOH at room temperature gave an orangered solution, from which a solid precipitated after the addition of two drops of NEt₃. Yellow crystals of (HNEt₃)₂[{UO₂- (L^1) ₄ $(\mu_2$ -OAc)₂]·CH₂Cl₂ were obtained after recrystallization from CH₂Cl₂/EtOH. The IR spectrum of the complex shows the $\nu_{\rm U=0}$ band at 910 cm⁻¹. A weak band at 1680 cm⁻¹ can be assigned as the $\nu_{\rm C=0}$ stretch of the acetato bridges. The $\nu_{\rm C=0}$ stretching frequency of the organic ligand appears in the complex at 1500 cm⁻¹. A bathochromic shift of 180 cm⁻¹ is observed in comparison to the position of this band in the uncoordinated H₂L¹. This indicates a chelate formation with a strong degree of electron delocalization. Such strong bathochromic shifts of the carbonyl frequencies have also been observed in benzoyl(N,N-dialkylthioureato) complexes with other metal ions.^{37,38,57,59} The absence of a band above 3000 cm⁻¹ indicates the deprotonation of the ligands during the complex formation, which is confirmed by the ¹H NMR spectrum of the compound, where no signals for the N–H protons are observed. A tetranuclear structure of the compound was confirmed by X-ray diffraction. The compound crystallizes in the triclinic space group $P\overline{1}$ with an asymmetric unit, which contains half of a complex molecule, one triethylammonium cation, and a half dichloromethane molecule. Figure 2 shows the structure of the $[{UO_2(L^1)}_4(OAc)_2]^{2-}$ anion.

The tetranuclear complex contains four uranyl units, four deprotonated $\{L^1\}^{2-}$ ligands, and two acetato ligands. Each uranyl moiety is coordinated equatorially by two *S*,*O*-bonded aroylthiourea units coming from two different ligands. This is a relatively rare coordination mode for uranyl ions, and a similar *S*,*O* chelate formation has hitherto been observed only for some complexes with monothiocarbamates, ^{83–85} heterocyclic thionates, ^{86,87} or substituted phosphine sulfides.⁸⁸ The high flexibility of the isophthaloylbis(thiourea) ligand allows the coordination of the equatorial coordination spheres of the uranyl cations in the present structure.

The coordination environments of the uranium atoms are pentagonal-bipyramids resulting from the *cis S,O*-coordination

distances						
U1-01	1.776(9)	C4-O5	1.27(2)	U2-O35	2.336(8)	
U1-O2	1.788(9)	C22-S21	1.71(2)	U2-072	2.415(8)	
U1-S1	2.844(4)	C22-N23	1.36(2)	C12-N13	1.36(2)	
U1-S21	2.841(4)	N23-C24	1.28(2)	N13-C14	1.28(2)	
U1-O5	2.275(8)	C24-O25	1.26(2)	C14-O15	1.26(2)	
U1-O25	2.339(8)	U2-011	1.76(1)	C32-N33	1.36(2)	
U1-071	2.402(8)	U2-012	1.78(1)	N33-C34	1.28(2)	
C2-S1	1.70(1)	U2-S11	2.847(4)	C34-O35	1.26(2)	
C2-N3	1.38(2)	U2-S31	2.844(8)	U1…U2	6.85(1)	
N3-C4	1.31(2)	U2-015	2.286(8)	U1…U2′	11.74(1)	
angles						
O1-U1-O2	178.5(4)	O1-U1-O25	88.9(4)	O1-U1-S1	90.3(4)	
O1-U1-O5	90.8(4)	O2-U1-O25	90.8(3)	O2-U1-S1	90.9(4)	
O1-U1-O71	92.9(4)	O2-U1-O5	90.8(4)	O1-U1-S21	88.7(7)	
O11-U2-O12	177.3(5)					

Table 1. Selected Bond Lengths (Å), Distances (Å), and Bond Angles (deg) in $(HNEt_3)_2[{UO_2(L^1)}_4(OAc)_2]^a$

of two deprotonated $\{L^1\}^{2-}$ ligands and an additional acetato ligand. Selected bond lengths and angles are listed in Table 1.

^{*a*}Symmetry operator: (') -x+1,-y+1,-z+1.

The uranyl bond lengths are between 1.776(1) and 1.788(9) Å, which is unexceptional and in line with published values.²¹ The O–U–O angles are 178.5(4) and 177.3(5)°. Two conformation types of the ligand are established in the $[{UO_2(L^1)}_4(OAc)_2]^{2-}$ anion: the linear conformation **A** and the hitherto unprecedented conformation **B** (Chart 2). The





bond lengths between the uranium atoms and the oxygen donor atoms of the organic ligand with the conformation **A** are around 2.28(1) Å and slightly shorter than the U–O bond lengths to the ligand with the conformation **B** with approximately 2.34(1) Å. The U–S bonds are almost equal with approximately 2.84 Å. The *S*,*O* chelate rings exhibit the typical extended delocalized π -systems with a slight elongation of the C–O and C–S bonds and a shortening of the C–N bonds, reflecting some double bond character.

To quantify the formation of two conformers of the organic ligand, DFT calculations on different conformations of H_2L^1 were performed (for details, see Supporting Information). They confirm conformation **A** as the most stable conformation with an energy difference of 28 kJ/mol to the conformation **B**. Such a small difference in energy does not prevent the formation of metal complexes with the other conformations but may explain the preference of **A** in most of the hitherto known compounds, where no additional intramolecular interactions play a role. This is slightly different in the $[{UO_2(L^1)}_4(OAc)_2]^{2-}$ anion, for which two interesting features are briefly discussed. As is illustrated in Figure 3a, the *S*,*O* chelate rings belonging to the conformation **B** strongly deviate from planarity (rms: 0.3556, maximum deviation for 0.543(7) Å for S21), while the *S*,*O* chelates resulting from the



Figure 3. (a) Chelate rings in the $[{UO_2(L^1)}_4(OAc)_2]^{2-}$ anion and (b) visualization of the $\pi-\pi$ interactions.

ligand with conformation **A** are planar with a maximum deviation of 0.210(9) Å for O5 (rms: 0.139). The latter values are in agreement with the situation in the chelate rings of other transition metal complexes with aroylthiourea ligands.^{36–49} Surprisingly, the distortions do not significantly influence the bond lengths inside the chelate rings and the previously mentioned C–N bond length equalization, but they allow additional weak attractive intramolecular π – π interactions via the central phenyl rings. The two rings are coplanar, and the C53–C53' distance is 3.31(3) Å (see Figure 3b).

Each two uranium atoms in the $[{UO_2(L^1)}_4(OAc)_2]^{2-}$ anion are linked by an acetato bridge. Their oxygen atoms occupy the fifth positions of the pentagonal bipyramidal coordination spheres of the metal atoms. The established bridge, however, is obviously not mandatory for the stabilization of the tetrameric complex. The reaction of $(NBu_4)_2[UO_2Cl_4]$ with H_2L^1 in EtOH gives a similar product but with EtO⁻/EtOH ligands instead of acetate ligands (see Scheme 3). The obtained orange-red precipitate has a composition of $(NBu_4)_2[{UO_2(L^1)}_4(OEt)_2(HOEt)_2]$. The IR spectrum of the product shows a broad signal at 3446 cm⁻¹, which can be assigned to O–H vibrations. The absence of a vibration at 3100 cm⁻¹ indicates the deprotonation of H_2L^1 .



Figure 4. Molecular structure of the $[{UO_2(L^1)}_4(OEt)_2(HOEt)_2]^{2-}$ anion.





The formation of a uranyl complex is confirmed by the presence of the strong band at 910 cm^{-1} . As in $(HNEt_3)_2[{UO_2(L^1)}_4(OAc)_2]$, a bathochromic shift of the $\nu_{C=0}$ stretch is observed. The presence of two (O–H) protons was confirmed by their ¹H NMR signal at 11.30 ppm. Single crystals of $(NBu_4)_2[\{UO_2(L^1)\}_4(OEt)_2(HOEt)_2]$ were obtained from a CH2Cl2/EtOH mixture. Unfortunately, due to unsatisfactory crystal quality, the refinement stopped at an R1 value of 0.11. Thus, a detailed discussion of the bond lengths and angles is not be done here. But, general bonding features and the molecular structure of the compound can certainly be derived. The coordination sphere of each uranyl moiety is completed by two S,O chelates and each one ethanolato and/ or one ethanol ligand. The previously discussed intramolecular $\pi - \pi$ interactions between the central phenyl units are also found in the $[{UO_2(L^1)}_4(OEt)_2(HOEt)_2]^{2-}$ anion, the structure of which is shown in Figure 4.

While the reactions of uranyl compounds with ligand H_2L^1 push the actinide into the less favored *S*,*O* coordination, the pyridine-centered ligands H_2L^2 provide more coordination modes, which may also include tri- or pentadentate arrangements, as is shown for the conformations **B** and **C** (see Chart 3). DFT calculations on H_2L^{2a} were performed to determine the preferred conformation of the ligand (for details, see Supporting Information). Unlike the situation at ligand H_2L^1 , the bifunctional conformation **A** is disfavored and the chelator-type conformations **B** and **C** are preferred. This preference may have to do with the opportunity of the formation of intramolecular hydrogen bonds, but it will at least support the formation of metal chelates under participation of the central pyridine ring.

At first, reactions of H_2L^{2a} and H_2L^{2b} with uranyl nitrate hexahydrate or uranyl acetate dihydrate were performed in MeOH at 50 °C without the addition of a supporting base. Such reactions ended in a decomposition of the ligands and the formation of dipicolinic acid. This hydrolysis product finally forms a hexanuclear uranyl complex of the composition $[UO_2(dipicolinate)(H_2O)]_6$ (see Scheme 3), which has already been described by Immirizi et al.⁸⁹ Obviously, the thiourea derivatives are sensitive against the strong acidic conditions in such solutions. Similar observations were made by Gatto during the reaction of a monosubstituted diacetylresorcinol thiosemicarbazone ligand and uranyl nitrate.⁹⁰ During the reaction, the C=N bond of the thiosemicarbazone was cleaved. The remaining ligand partially hydrolyzed under formation of 4,6-diacetylresorcinol, which coordinated to the uranyl ions under the formation of a tetrameric, macrocyclic compound.

The decomposition of H_2L^{2a} and H_2L^{2b} can be avoided when a supporting base is added. This allows the deprotonation of the ligands and their coordination in favor of their hydrolysis. Chelate coordination of $\{L^{2a}\}^{2-}$ and $\{L^{2b}\}^{2-}$ with uranyl ions was obtained when two drops of triethylamine were added to the reaction mixtures. A compound of the composition $[UO_2(L^{2a})(MeOH)]$ was obtained from the reaction of H_2L^{2a} , a uranyl source such as $[UO_2(CH_3COO)_2] \cdot 2H_2O$, $(NBu_4)_2[UO_2Cl_4]$, or $[UO_2(NO_3)_2] \cdot 6H_2O$ and NEt₃ in methanol. Slow evaporation of the reaction mixtures at room temperature gave single crystals of the compound (Scheme 3). Dissolution of the complex in a coordinating solvent such as DMF led to an exchange of the coordinated methanol ligand, and $[UO_2(L^{2a})$ - (DMF)]·(DMF) was obtained after the slow evaporation of the solvent at room temperature. The IR spectrum of $[UO_2(L^{2a})(MeOH)]$ shows the strong asymmetric $\nu_{II=O}$ band at 912 cm⁻¹ and the ν_{OH} band at 3211 cm⁻¹, while the spectrum of $[UO_2(L^{2a})(DMF)] \cdot (DMF)$ shows the $\nu_{U=0}$ stretch at 904 cm⁻¹. The carbonyl bands appear at 1654 cm^{-1} for $[UO_2(L^{2a})(MeOH)]$ and at 1629 cm^{-1} for $[UO_2(L^{2a})(DMF)] \cdot (DMF)$. This corresponds to a bathochromic shift of only 26 and 51 cm⁻¹ with respect to the values in H_2L^{2a} . These values strongly indicate that the C=O functionality is not involved in the coordination. The absence of the N-H vibration suggests the deprotonation of the ligand, which is confirmed by the ¹H NMR spectrum. The ESI+ mass spectra show the fragments $[{M-solv}+K]^+$ at m/z = 702.1331and $[{M-solv}+Na]^+$ at m/z = 686.1625. Interestingly, the cluster fragments [{M-solv}₂+K]⁺ at 1365.3036 and [{Msolv}₂+Na]⁺ at 1349.3322 were observed. Figure 5 shows the



Figure 5. Molecular structures of (a) $[UO_2(L^{2a})(MeOH) \text{ and } (b) [UO_2(L^{2a})(DMF)]$. Hydrogen atoms except for the coordinated methanol were omitted for clarity.

molecular structures of $[UO_2(L^{2a})(MeOH)]$ and $[UO_2(L^{2a})-(DMF)]$. Selected bond lengths and angles are given in Table 2. The uranium atoms in both structures have a distorted hexagonal-bipyramidal coordination sphere with the oxido ligands in the axial positions. The ligands $\{L^{2a}\}^{2-}$ coordinate pentadentate with three nitrogen and two sulfur atoms. The hexagonal base is completed by the coordination of a solvent molecule. The uranyl bond lengths with values between 1.748(7) and 1.782(2) Å and with O=U=O bond angles of 178.1(1) and 178.2(3)° are unexceptional. The U–N bond lengths are in the range of 2.438(3)–2.514(8) Å for the thiourea sites and between 2.600(3) and 2.624(7) Å for the pyridine rings.

Reactions of H_2L^{2b} with uranyl acetate or $(NBu_4)_2[UO_2Cl_4]$ in the presence of 2 drops of triethylamine give yellow precipitates, which were recrystallized from a 1:1 mixture of $CH_2Cl_2/MeOH$ (v/v) and characterized as $[UO_2(L^{2b})(H_2O)]$ (Scheme 2). $[UO_2(L^{2b})(H_2O)]$ shows the same coordination

Table 1	2. Selected	Bond I	Lengths	(A)	and	Angles	(deg)	in
$[UO_2(]$	L ^{2a})(MeOH	I)], [UC	$D_2(\tilde{L}^{2a})($	DMI	F)],	•		
ĨUO,	$(L^{2b})(H_{1}O)$]. and []	$UO_{2}(L^{2b})$	')(D	MF)	a		

	$[UO_2(L^{2a}-) (MeOH)]$	$[UO_2(L^{2a})-(DMF)]$	$[UO_2(L^{2b})- (H_2O)]]$	[UO ₂ (L ^{2b})- (DMF)]		
U1-01	1.776(2)	1.748(7)	1.772(3)	1.768(5)		
U1-O2	1.782(2)	1.760(6)	1.779(3)	1.758(5)		
U1-S1	2.9796(9)	2.939(2)	2.882(1)	2.924(2)		
U1-S11	2.9685(9)	2.913(3)	2.933(1)	2.932(2)		
U1-N3	2.508(3)	2.514(8)	2.512(3)	2.512(5)		
U1-N13	2.438(3)	2.515(8)	2.538(3)	2.536(6)		
U1-N26	2.600(3)	2.624(7)	2.601(3)	2.608(5)		
U1-O31	2.490(2)	2.440(6)	2.490(3)	2.435(5)		
O1-U1-O2	178.1(1)	178.2(3)	179.7(1)	179.6(5)		
O31-U1-S1	66.44(6)	65.4(2)	64.72(8)	64.9(1)		
O31-U1-N3	121.31(8)	120.3(2)	120.7(1)	120.3(2)		
O31-U1-N26	161.61(8)	168.8(2)	165.1(1)	166.5(2)		
O31-U1-N13	122.19(8)	120.3(2)	120.6(1)	121.0(2)		
O31-U1-S11	66.94(6)	65.2(2)	64.72(8)	65.9(1)		
N26-U1- N3	60.32(8)	61.1(2)	61.0(1)	60.4(2)		
N26 –U1-S1	114.06(6)	114.3(2)	114.93(8)	114.6(1)		
N26-U1-N13	60.68(9)	61.1(2)	60.9(1)	61.1(2)		
N26-U1-S11	114.67(6)	114.2(2)	114.93(8)	114.2(1)		
arrhy structure like and some of the latter transformer of the latter						

"The atomic labeling scheme of the latter two compounds has been adopted from the $\{L^{2a}\}^{2-}$ complexes in Figure 5.

mode as is observed in $[UO2(L^{2a})(MeOH)]$ with a coordinated water molecule instead of methanol. $[UO_2(L^{2b})-(H_2O)]$ crystallizes in the orthorhombic space group *Pbca*. Also here, the water molecule can be replaced by the dissolution of the compound in DMF. The resulting $[UO_2(L^{2b})(DMF)]$ crystallizes in the monoclinic space group $P2_1/c$. The structures of the complexes with the $\{L^{2b}\}^{2-}$ ligand are virtually identical to those with the diethyl amine-substituted ones. Thus, no extra figures are included with the molecular structures of these compounds. They can be found in the Supporting Information. Selected bond lengths and angles, however, are compared with the values obtained for $[UO_2(L^{2a})(MeOH)]$ and $[UO_2(L^{2a})(DMF)]$ in Table 2.

Similarly to the complexes with $\{L^{2a}\}^{2-}$, analyses of the mass spectra of the mononuclear complexes $[UO_2(L^{2b})(H_2O)]$ and $[UO_2(L^{2b})(DMF)]$ indicate the loss of the solvent molecules during the measurements and the formation of dimeric fragments $[\{M-(solv)\}_2+Na]^+$ with a mass peak at m/z =1405.2538 and even trimeric fragments $[\{M-(solv)\}_3+Na]^+$ (m/z = 2096.3828). Although the structures of the resulting complexes formed in the gas phase are not clear, their formation describes the trend of such compounds to form oligomeric units.

Oligomerization of the mononuclear uranyl complexes is also observed, when the reaction of uranyl salts is done with an equivalent amount of H_2L^2 or when the $[UO_2(L^2)(MeOH/H_2O)]$ complexes are treated with an additional amount of NEt₃. This is exemplarily discussed for $(HNEt_3)_2[{UO_2(L^{2a})}-(\mu_2 \cdot OMe)]_2]$, which was obtained as a yellow solid from the treatment of a solution of $[UO_2(L^{2a})(MeOH)]$ in methanol with two drops of NEt₃. The IR spectrum of the compound shows the absence of NH vibrations, which confirms the deprotonation of the organic ligand in the compound. A strong absorption observed at 1589 cm⁻¹ can be assigned to the $\nu_{C=O}$ stretching vibration. In comparison, the $\nu_{C=O}$ stretch of the noncoordinated ligand is observed at 1680 cm⁻¹, and the $\nu_{C=O}$ stretch of the monomeric complex $[(UO_2(L^{2a})(MeOH))]$ is observed at 1654 cm⁻¹. The significant bathochromic shift strongly suggests the coordination via the carbonyl oxygen atoms. Similar shifts have also been observed for other metal complexes after chelate formation of H_2L^{2a} , which indicates strong electron delocalization inside the chelate rings.^{60,61} The presence of uranyl ions is confirmed by $\nu_{U=0}$ stretching vibrations observed at 912 cm⁻¹.

Yellow crystals suitable for X-ray diffraction analysis were obtained from a 1:1 mixture of CH₂Cl₂/MeOH (v:v) at room temperature. The analysis of the X-ray data as well as the results of the elemental analysis confirm the composition of the complex as (HNEt₃)₂[{UO₂(L^{2a})(μ_2 -OMe)}₂]. Figure 6 shows the structure of the complex anion [{UO₂(L^{2a})(μ_2 -OMe)}₂]²⁻. Selected bond lengths and angles are listed in Table 3.



Figure 6. Structure of the complex anion of $(HNEt_3)_2[{UO_2(L^{2a})(\mu_2 - OMe)}_2]$ with a depiction of the found *syn,syn*-arrangement of the methanolato ligands and the sulfur atoms of the thiourea units. Hydrogen atoms were omitted for clarity.

Table 3. Selected Distances (Å) and Angles (deg) in *syn,syn*- $(HNEt_3)_2[{UO_2(L^{2a})(\mu_2-OMe)}_2]$

U1-01	1.765(6)	U2-011	1.776(6)
U1-O2	1.770(6)	U2-012	1.783(6)
U1-O5	2.357(6)	U2-O25	2.380(6)
U1-015	2.376(5)	U2-O35	2.372(6)
U1-N46	2.579(7)	U2-N56	2.564(7)
U1-061	2.348(6)	U2-O61	2.336(6)
U1-O62	2.365(5)	U2-O62	2.344(5)
U1…U2	3.772(5)		
O1-U1-O2	178.5(3)	O11-U2-O12	179.0(3)
O1-U1-N46	90.7(3)	O11-U2-N46	91.4(3)
O1-U1-O5	89.1(3)	O11-U2-O25	88.2(3)
O1-U1-O15	89.6(3)	O11-U2-O35	91.6(3)
O1-U1-O61	91.2(3)	O11-U2-O61	91.7(3)
O1-U1-O62	89.5(3)	O11-U2-O62	90.4(2)

The structure of $[{UO_2(L^{2a})(\mu_2-OMe)}_2]^{2-}$ consists of two uranyl units, which are coordinated by each one *O*,*N*,*O*-

bonded $\{L^{2a}\}^{2-}$ ligand. The subunits are connected by two methanolato ligands. Thus, each uranium atom is sevenfold coordinated with a pentagonal-bipyramidal geometry. The uranyl bond lengths are in the range of 1.765(6)-1.783(6) Å. The U–O bond lengths in the equatorial plane are in the range of 2.348(6)-2.376(5) Å, while the U–N bonds are between 2.579(7) and 2.564(7) Å. The carbonyl bonds of 1.31(1) Å are significantly longer than the distance of 1.223(5) Å, which is observed in the noncoordinated ligand H_2L^{2a} and therefore in the expected range for chelate complexes. The equatorial positions of the pentagonal-bipyramidal coordination spheres of the uranium atoms are almost perfectly planar. The maximum deviation from the equatorial mean least-squares plane of 0.142 Å is observed for N46.

An interesting structural feature of the $[{UO_2(L^{2a})(\mu_2 - OMe)}_2]^{2-}$ anion is the orientation of the bridging methanolato ligands and the sulfur atoms with regard to the equatorial plane. Both point to the same direction and, thus, form the *syn,syn*-conformer of the complex as is depicted in Figure 6.

The experiments described above show that the $[{UO_2(L^2)}-$ (solv)] complexes are not stable in solution and readily replace their H₂O or MeOH ligands. Even a complete rearrangement of the coordination mode of the $\{\tilde{L^2}\}^{2-}$ ligands from pentadentate S,N,N,N,S chelates to an O,N,O coordination was observed during the formation of the $[{UO_2(L^2)(\mu_2 - \mu_2)}]$ $OMe)_{2}^{2-}$ anions, and also, the latter dimeric ions seems to be unstable in solutions. This was first concluded from the ¹H NMR spectra of the compound measured in CDCl₃ and $(CD_3)_2$ SO. The signals of the deprotonated ligand $\{L^{2a}\}^{2-}$ and the signals corresponding to the counterions $\{HNEt_3\}^+$ were readily observed in both solvents. Those of the bridging methanolato ligand, however, could not be resolved in CDCl₃. This may indicate a decomposition of the dimeric complex in solution, the formation of (most probably monomeric) species with solvent molecules (e.g., MeOH, H₂O). The missing signal for the coordinated methanolato ligands indicates a fast exchange with other donor ligands (e.g., OH^-/H_2O). The ¹H NMR spectrum of $(HNEt_3)_2[{UO_2(L^{2a})(\mu_2-OMe)}_2]$ in $(CD_3)_2$ SO, however, shows a signal at 3.13 ppm, which can be assigned to noncoordinated methanol, resulting from a complete replacement of these ligands in the coordination sphere of uranium. These findings are supported by the negative-mode ESI mass spectrum of the complex, which has been measured in CHCl₃/MeOH. The peak of the molecular ion $[{UO_2(L^{2a})(\mu_2 \text{-}OMe)}_2]^{2-}$ was not observed, but different peaks were observed, which indicate the decomposition of the complex in solution or in the gas phase. The two main peaks observed at m/z = 680.1775 and 694.1932 can be assigned to the monomeric anions $[UO_2(L^{2a})(OH)]$ and $[UO_2(L^{2a})-$ (OMe)].

The spectroscopic results are supported by the isolation of orange-yellow crystals from a methanol/DMSO mixture of $(HNEt_3)_2[{UO_2(L^{2a})(\mu_2-OMe)}_2]$. They consist of a mononuclear compound of the composition $[UO_2(L^{2a})(DMSO)_2]$ as could be confirmed by a preliminary X-ray diffraction study. The quality of the single crystals, however, was not suitable for a detailed discussion of the bond lengths and angles. But the molecular structure of the compound could be derived unambiguously. It is shown in Figure 7. The $\{L^{2a}\}^{2-}$ ligand coordinates tridentate to the uranyl unit through an *O*,*N*,*O* donor set and the coordination environment of the uranyl unit is completed by two *O*-bonded dimethyl sulfoxide ligands.



Figure 7. Molecular structure of $[UO_2(L^{2a})(DMSO)_2]$.

Although the central pyridine ring of H_2L^2 considerably changes the coordination properties of the bipodal aroylthiourea ligands with uranyl ions compared to the behavior of H_2L^1 , the resulting complexes suffer from an inherent instability, which is caused by the coordination of additional solvent ligands and/or the pH-dependent formation of binuclear species. A more stable complex is formed with H_2L^3 , which has a central bipyridine unit and, thus, should be able to act as a hexadentate ligand.

Reactions of H_2L^3 with uranyl acetate or $(NBu_4)_2[UO_2Cl_4]$ in the presence of 2 drops of triethylamine give yellow precipitates of $[UO_2(L^3)]$ with yields of about 90%. The IR spectrum of the product shows a strong $\nu_{U=0}$ vibration at 908 cm⁻¹ and the $\nu_{C=0}$ stretch is detected at 1637 cm⁻¹. The latter frequency corresponds to a bathochromic shift of 70 cm⁻¹ with respect to the value in H_2L^3 , which is slightly more than the shift observed between $[UO_2(L^{2a})(MeOH)]$ and H_2L^{2a} . The observed shift does not necessarily imply that the coordination is established via the carbonyl group because in such cases the bathochromic shift of the carbonyl band is more considerable with values larger than 100 cm^{-1} .^{60,61} Nevertheless, a strong electron delocalization involving the C=O group is indicated. The absence of an NH vibration suggests the deprotonation of the coordinated ligand. The positive-mode ESI mass spectrum shows the expected molecular fragments $[M + H]^+$ at m/z =741.1991, $[M + Na]^+$ at m/z = 763.1816 and $[M + K]^+$ at m/z= 779.1550. No dimerization or trimerization was detected, indicating a higher stability of the compound compared to the chelates formed with H₂L².

Single crystals suitable for X-ray analysis were obtained from a solution of a 1:1 mixture of CH₂Cl₂/MeOH (v/v). Figure 8 shows the molecular structure of $[UO_2(L^3)]$. Selected bond lengths and angles are listed in Table 4. Expectedly, the organic ligand coordinates as a hexadentate ligand to the uranyl moiety via four nitrogen and two sulfur atoms, giving a hexagonalbipyramidal coordination of the metal ion. The uranyl bond lengths are 1.769(2) and 1.772(2) Å and the O=U=O bond angle is 176.0(1). The hexagonal plane of $[UO_2(L^3)]$ is almost perfectly planar, with a maximum deviation of 0.17 Å for atom N3 from the mean least-squares plane formed by the donor atoms of the equatorial plane of U1. The U-N bond lengths are between 2.517(3) and 2.518(3) Å for the thiourea sites and 2.609(3) and 2.610(3) Å for the bipyridine nitrogen atoms. The U–S distances are 2.88(1) Å. This value is 0.05 Å shorter than the value of the U-S bond lengths observed in $[UO_2(L^{2a})(MeOH)]$, where $\{L^{2a}\}^{2-}$ shows the same coordination pattern. However, it is equal to the value of the U-S



Figure 8. Molecular structure of $[{UO_2(L^3)}]$. Hydrogen atoms were omitted for clarity.

distances observed in the compound $(NBu_4)_2[\{(UO_2(L^1))_4-(OAc)_2]$ with $\{L^1\}^{2-}$ showing the S,O coordination pattern.

Liquid-liquid extraction processes play an important role in the treatment of actinides and other heavy metals in waste solutions and in recovery procedures. Well-established solvent extraction methods for nuclear fuel recovery are processes such as PUREX (plutonium and uranium recovery by extraction), TALSPEAK (trivalent actinides lanthanides separation by phosphorus-reagent extraction from aqueous complexes), or SANEX (selective actinide extraction).⁹¹⁻⁹³ Most of the ligands used in such separation processes are phosphorusbased derivatives, but research on the development of new ligand systems to optimize selective extraction and back extraction of actinides from their lanthanide counterparts is still ongoing. Recently, a variety of ligand systems based on the 2,6-pyridine and 6,6'-(2,2'-bipyridine) scaffolds were successfully studied as extractants in the above-mentioned methods.^{94,95}

To prove the potential suitability of the ligands discussed above as possible extraction agents for uranyl ions, the stability of $(HNEt_3)_2[\{UO_2(L^1)\}_4(OAc)_2]$, $[UO_2(L^{2a})(MeOH)]$, $[UO_2(L^{2b})(H_2O)]$, and $[UO_2(L^3)]$ in aqueous solutions was studied. For this, CH_2Cl_2 solutions of the complexes were mixed with the aliquots of aqueous solutions, the pH values of which were adjusted with nitric acid. After vigorous shaking for 30 min, the phases were separated, and the distribution of the uranyl ions between the two phases were determined radiometrically.

 $(HNEt_3)_2[{UO_2(L^1)}_4(OAc)_2], [UO_2(L^{2a})(MeOH)], and [UO_2(L^{2b})(H_2O)]$ are not stable in acidic aqueous solutions. They rapidly decompose, and the released uranyl ions move to the aqueous phase. Optically, in the case of the complexes $[UO_2(L^{2a})(MeOH)]$ and $[UO_2(L^{2b})(H_2O)]$, the solvent mixtures became turbid, which indicates the formation of less soluble hydrolyzed species.

The extraction of uranyl ions into the aqueous phase increases with decreasing pH (see Figure 9). (HNEt₃)₂[{UO₂(L¹)}₄(OAc)₂], where the uranyl ion is bounded via the bidentate *S*,*O* coordination, is the most unstable complex with a uranyl nitrate formation of 60% already at pH 7 and 98% at pH 1. The monomeric complexes [UO₂(L^{2a})-(MeOH)] and [UO₂(L^{2b})(H₂O)] show a similar behavior with extraction rates at neutral pH of around 20% and >70% at pH 1. Such a behavior is not unexpected, keeping in mind the reaction of H₂L² with uranyl nitrate, which results in an immediate ligand cleavage and the formation of

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[UO_2(L^3)]$ bond lengths U1-01 1.769(2)U1-N13 C4-05 1.232(4)2.518(3)U1-02 1.772(3)U1-N26 2.609(3)1.229(4)C14-O15 U1-S1 2.88(1)U1-N36 2.610(3) 1.380(5)C2-N3 U1-S11 2.88(1)C2-S1 1.706(4)C4-N3 1.346(5)1.718(4)1.370(5)U1-N3 2.517(3)C12-S11 C12-N13 C14-N13 1.353(5)bond angles O1-U1-O2 176.0(1)N13-U1-S1 120.0(7)O1-U1-N13 87.0(1) 01-U1-N36 92.0(1) 01-U1-N26 83.0(1) O2-U1-N13 92.0(1) O2-U1-N36 85.0(1) O2-U1-N26 93.0(1) N13-U1-N36 61.8(9) N3-U1-S11 119.9(7)O1-U1-S1 88.9(9) O1-U1-S11 94.5(9) N3-U1-N26 62.0(9) O2-U1-S1 93.9(8) O2-U1-S11 89.4(9)



Figure 9. (a) Uranyl extraction from the synthesized complexes into an aqueous nitric acid solution at different pH values. Concentration of the complexes: 0.4 mM (in CH_2Cl_2); T = 23 °C. (b) pH dependence of the uranyl extraction from $[UO_2(L^3)]$ at high acidic concentrations.

 $[UO_2(dipicolinate)(H_2O)]_6$ (vide supra). More stable is $[UO_2(L^3)]$. It shows almost no release of the metal ion from pH 7 to pH 1 with extraction values $\leq 1\%$ (see Figure 9). The formation of uranyl ions from the organic phase of $[UO_2(L^3)]$ was observed only at high acid concentrations. In half-concentrated HNO₃ solution, a uranyl extraction of 80% was observed after 30 min. A complete extraction of the uranyl ions

from $[UO_2(L^3)]$ was obtained in concentrated nitric acid (Figure 9).

The release of the uranyl ions from the ligand frameworks was also monitored spectroscopically with ¹H NMR and UV/ vis. A comparison of the UV/vis spectra of the organic and aqueous phases before and after the extraction procedure clearly show that the extracted uranium species are not

identical with the used chelates $(HNEt_3)_2[\{UO_2(L^1)\}_4$ $(OAc)_2]$, $[UO_2(L^{2a})(MeOH)]$ or $[UO_2(L^{2b})(H_2O)]$. This behavior was confirmed by the ¹H NMR spectra. In contrast, the spectra of the extracted organic phase of $[UO_2(L^3)]$ from pH 7 to 1 show no differences to the spectrum of the $[UO_2(L^3)]$. Decomposition was observed only in the spectra of solutions with high acid concentrations.

CONCLUSIONS

A series of uranyl complexes with three types of bifunctional aroylbis(N,N-dialkylthiourea) ligands was prepared and characterized spectroscopically and by X-ray diffraction. Mono-, di-, and tetranuclear compounds obtained from the phenyl- or pyridine-centered ligands (H_2L^1 and H_2L^2) are labile and readily undergo ligand exchange reactions or hydrolysis. Remarkably stable is the neutral complex [$UO_2(L^3)$] with the bipyridine-centered ligand. This complex does not decompose even under moderately acidic conditions. Preliminary experiments indicate that H_2L^3 does not form stable complexes with lanthanides, which recommends further experiments concerning selective uranium extraction from lanthanide/uranium mixtures. Such studies are currently being done in our laboratory.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b01918.

Ellipsoid representations of the complexes, tables containing X-ray data, structural parameters, and details on DFT calculations and the extraction experiments (PDF)

Accession Codes

CCDC 1549621–1549627 and 1851629 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, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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