Coordination chemistry of 2,2′-biphenylenedithiophosphinate and diphenyldithiophosphinate with U, Np, and Pu†

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New members of the dithiophosphinic acid family of potential actinide extractants were prepared: heterocyclic 2,2′-biphenylenedithiophosphinic acids of stoichiometry HS2P(R2C12H6) (R = H or tBu). The time- and atom-efficient syntheses afforded multigram quantities of pure HS2P(R2C12H6) in reasonable yields (≈60%). These compounds differed from other dialkyldithiophosphinic acid extractants in that the two aryl groups were connected to one another at the ortho positions to form a 5-membered dibenzophosphole ring. These 2,2′-biphenylenedithiophosphinic acids were readily deprotonated to form S2P(R2C12H6)1− anions, which were crystallized as salts with tetraphenylporphinium cations (ZPh4+; Z = P or As). Coordination chemistry between [S2P(tBu2C12H6)1−] and [S2P(C6H5)11−] with U, Np, and Pu was comparatively investigated. The results showed that dithiophosphinate complexes of UIV and NpIV were redox stable relative to those of UIII, whereas reactions involving PuIV gave intractable material. For instance, reactions involving UIV and NpIV generated An[S2P(tBu2C12H6)4] whereas reactions between PuIV and [S2P(C6H5)1]− generated a mixture of products from which we postulated a transient PuIII species based on UV-Vis spectroscopy. However, the trivalent Pu[S2P(C6H5)2]3(NC5H5)2 compound is stable and could be isolated from reactions between [S2P(C6H5)1]− and the trivalent PuI3(NC5H5)4 starting material. Attempts to synthesize analogous trivalent compounds with UIV provided the tetravalent U[S2P(C6H5)2]4 oxidation product.

Introduction

There exists considerable interest in solving longstanding problems associated with the indefinite on-site storage of spent fuel at nuclear power plants. Minor actinide (Am, Cm) partitioning and transmutation has emerged as one attractive proposition for achieving this goal.1−5 In this approach, the minor actinides are separated (partitioned) from fission products in the spent fuel and converted (transmutated) to short-lived isotopes in fast breeder reactors. Partitioning and transmutation is attractive because it recycles the spent fuel and allows additional energy to be harnessed from the nuclear transmutation processes. Unfortunately, several technical challenges currently prevent the implementation of partitioning and transmutation strategies on an industrial scale. Perhaps the most daunting chemical problem is associated with the partitioning of fissionable minor actinides from the lanthanide fission products. This separation is particularly challenging because in general both minor actinides and lanthanides form hard, oxophilic, trivalent ions that share similar chemical and physical properties.6−9

Of the separation strategies proposed previously,1,10−17 liquid/liquid extraction tactics relying on dithiophosphinic acids (HS2PR2) have emerged as a promising solution to the partitioning problem.8,18−25 For example, HS2P(o-CF3C6H4)2 gives the largest Am/Eu separation factor (SF) of any extractant reported to date (SFAm/Eu = 100 000).19 Although many variables influence the extraction process, the large separation factors observed for HS2P(o-CF3C6H4)2 are thought to be a consequence of greater covalency in the Am–S2PR2 interactions.
vs. the more ionic Eu–S\textsubscript{2}PR\textsubscript{2} interactions.\textsuperscript{18,26} Recent structural, spectroscopic, and theoretical studies of a series of S\textsubscript{2}PR\textsubscript{2}\textsuperscript{1–} anions (R = Me, C\textsubscript{6}H\textsubscript{5}, p-C\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{4}, m-C\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{4}, o-C\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{4}, o-MeC\textsubscript{6}H\textsubscript{4}, o-MeOC\textsubscript{6}H\textsubscript{4}) revealed that the Am/Eu separation factors were correlated with the extent and nature of π-mixing between the aryl groups and the PS\textsubscript{2}\textsuperscript{1–} core of the dithiophosphinate extractant.\textsuperscript{27} These studies identified that π-mixing depended on the rotameric orientation of the aryl rings, with larger separation factors seen when the rotation of the aryl groups was restricted. Hence, our recent efforts have focused on further optimizing this enatic state\textsuperscript{28} for more selective actinide binding by constraining the aryl ring orientations through C–C linkages (Scheme 1).

Reported herein is the first in a series of synthetic studies describing the preparation of heterocyclic dithiophosphinic acids with tethered aryl groups – specifically those that contain the 5-membered dibenzo phosphole ring. These efforts include the preparation of the 2,2′-biphenylenedithiophosphinic acids, HS\textsubscript{2}P(R\textsubscript{2}C\textsubscript{12}H\textsubscript{8}) (R = H or ‘Bu), and their conjugate bases, S\textsubscript{2}P(R\textsubscript{2}C\textsubscript{12}H\textsubscript{8})\textsuperscript{1–}, which were isolated as salts with tetraphenylphosphonium cations (ZPh\textsubscript{4}\textsuperscript{+}; Z = P or As). Additionally, the coordination chemistry of the 2,2′-biphenylenedithiophosphinate anions with uranium, neptunium, and plutonium has been explored in comparison to that of the untethered diphenyldithiophosphinate ion, S\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}\textsuperscript{1–}. These reactivity studies provided a useful platform for evaluating how actinide coordination chemistry with dithiophosphinic acids with tethered aryl groups specifically those that contain the 5-membered dibenzo phosphole derivatives, and intractable mixtures formed instead. We found, however, that addition of elemental sulfur directly to the halophosphines involves reduction to the corresponding phosphine and a subsequent treatment with elemental sulfur, followed by the addition of either ammonium carbonate or ammonium hydroxide.\textsuperscript{19,21,27,30} Unfortunately, in our laboratories, this methodology failed when applied to the dibenzo[b,d]phosphole derivatives, and intractable mixtures formed instead. We found, however, that addition of elemental sulfur directly to the halophosphine (which presumably generates the thiophosphinyl halide) followed by addition of sodium hydrosulfide hydrate (NaSH·xH\textsubscript{2}O) and aqueous workup cleanly provided the desired 2,2′-biphenylenedithiophosphinic acid, HS\textsubscript{2}P(C\textsubscript{12}H\textsubscript{8})\textsubscript{3}, in 54% overall yield from Br\textsubscript{2}C\textsubscript{12}H\textsubscript{8}.

This ‘one-pot’ sulfurization method has several advantages over prior approaches. The purification protocol was simple and avoided issues resulting from the instability of dithiophosphinic acids toward hydrolysis or thermolytic conversion (with loss of H\textsubscript{2}S) to the corresponding anhydro-sulfide. Undesired reaction byproducts and unreacted starting materials were also easily removed by distillation under vacuum, filtration, or washing with hexane. Moreover, this atom-efficient method avoided additional reduction steps, could be carried out in approximately one day, and resulted in good yields on multi-gram scales.

**Results and discussion**

**Syntheses of HS\textsubscript{2}P(R\textsubscript{2}C\textsubscript{12}H\textsubscript{8}) (R = H, ‘Bu)**

The compound 2,2′-biphenylenedithiophosphinic acid, HS\textsubscript{2}P-(C\textsubscript{12}H\textsubscript{8}), was prepared as described in eqn (1) and (2).

1. 1/8 S\textsubscript{2}, toluene, 110 °C
2. NaSH·xH\textsubscript{2}O (2 eq.), H\textsubscript{2}O\textsubscript{2} (1 eq.), H\textsubscript{2}O, 90 °C
3. H\textsubscript{2}O

The synthetic procedure began with treating the commercially available 2,2′-dibromobiphenyl, Br\textsubscript{2}C\textsubscript{12}H\textsubscript{8}, with two equivalents of n-butyllithium to generate the known 2,2′-dibenthiodiphosphole compound, Li\textsubscript{2}(C\textsubscript{12}H\textsubscript{8}).\textsuperscript{29} This organolithium reagent has been reported to react with phosphorus trichloride to generate 5-chloro-5H-dibenzo[b,d]phosphole in good yield.\textsuperscript{29} In our hands, this reaction afforded a second product that was characterized by \textsuperscript{31}P NMR spectroscopy as 5-bromo-5H-dibenzo[b,d]phosphole, such that the chloro- to bromophosphole ratio was approximately 3 : 2 (eqn (1)). This interpretation was supported by similar halogen exchange reactions noted during the preparation of some closely related compounds.\textsuperscript{19} It was not necessary to separate the 5-chloro-5H-phosphole from the 5-bromo-5H-phosphole, as both halophosphines behaved similarly in the subsequent conversion to the dithiophosphinic acid.

The usual method to prepare dithiophosphinic acids from halophosphines involves reduction to the corresponding phosphine and a subsequent treatment with elemental sulfur, followed by the addition of either ammonium carbonate or ammonium hydroxide.\textsuperscript{19,21,27,30} Unfortunately, in our laboratories, this methodology failed when applied to the dibenzo[b,d]phosphole derivatives, and intractable mixtures formed instead. We found, however, that addition of elemental sulfur directly to the halophosphine (which presumably generates the thiophosphinyl halide) followed by addition of sodium hydrosulfide hydrate (NaSH·xH\textsubscript{2}O) and aqueous workup cleanly provided the desired 2,2′-biphenylenedithiophosphinic acid, HS\textsubscript{2}P(C\textsubscript{12}H\textsubscript{8}), in 54% overall yield from Br\textsubscript{2}C\textsubscript{12}H\textsubscript{8}.

![Scheme 1](image-url)
Similar methodology was used to prepare the di-tert-butyl substituted derivative, 4,4′-di-tert-butyl-2,2′-biphenylenedithiophosphinic acid, HS₂P(′Bu₂C₁₂H₈), as illustrated in eqn (3) and (4).

The synthesis relied on previous work that had established that 4,4′-di-tert-butylbiphenyl, ′Bu₂C₁₂H₈, could be deprotonated at the 2 and 2′ positions with Schlosser's base, ′BuLi/KO′Bu. We found that the in situ generated organometallic dianion reacted smoothly with phosphorus trichloride to afford 3,7-di-tert-butyl-5-chloro-5H-dibenzo[b,d]phosphole, ClP(′Bu₂C₁₂H₈). Treatment of the chlorophosphole with elemental sulfur and sodium hydrosulfide hydrate (as discussed above) afforded the 4,4′-di-tert-butyl-2,2′-biphenylenedithiophosphinic acid, HS₂P(′Bu₂C₁₂H₈), cleanly in 52% overall yield from the commercially available 4,4′-di-tert-butylbiphenyl.

The solubility of dithiophosphinic acids is important for their use as ligands and as extractants in liquid/liquid separations. Our qualitative observations suggested that after isolation as a microcrystalline solid the unsubstituted acid, HS₂P(C₁₂H₈), was only moderately (<20 mg mL⁻¹) soluble in halogenated solvents (chloroform and dichloromethane) and was essentially insoluble in acetonitrile, toluene, tetrahydrofuran, diethyl ether, and n-hexane. In contrast, the substituted analogue, HS₂P(′Bu₂C₁₂H₈), readily dissolved in all of these solvents except n-hexane. We anticipate that the more soluble acid, HS₂P(′Bu₂C₁₂H₈), is better suited for use as an actinide ligand and as an extractant in liquid/liquid separation schemes.

Syntheses and structures of [ZPh₄][S₂P[R₂C₁₂H₈]] (R = H, ′Bu; Z = As, P)

The HS₂P(C₁₂H₈) and HS₂P(′Bu₂C₁₂H₈) acids were readily deprotonated with aqueous NH₄OH in air as shown in eqn (5) and (6). Subsequent addition of tetraphenylpnictonium chloride [ZPh₄Cl, Z = P or As) provided the [ZPh₄][S₂P(R₂C₁₂H₈)] salts in reasonable crystalline yields ranging from 41 to 45%.

Single crystals of [PPh₄][S₂P(C₁₂H₈)] and [AsPh₄][S₂P(′Bu₂C₁₂H₈)] suitable for X-ray diffraction studies were grown by slow evaporation of acetone/water solutions. We note that single crystals of [PPh₄][S₂P(′Bu₂C₁₂H₈)] were also obtained, but the disorder associated with the S₂P(′Bu₂C₁₂H₈)¹⁻ anions prevented the generation of a meaningful structural model. The structural metrics for [PPh₄][S₂P(C₁₂H₈)] and [AsPh₄][S₂P(′Bu₂C₁₂H₈)] were similar, as is evident from the molecular structures shown in Fig. 1 and 2 and selected bond distances and angles summarized in Tables 1 and 2. The solid-state data confirmed that these dithiophosphinates contained a planar...
dibenzophosphole unit. In both [PPh₄][S₂P(C₁₂H₈)] and [AsPh₄][S₂P(tBu₂C₁₂H₆)], the central phosphorus atom was almost exactly in the plane defined by the biphenylene carbon atoms, with deviations of 0.002 and 0.048 Å, respectively. The S₂P(R₂C₁₂H₆)⁻ anions had a nearly ideal C₂ᵥ symmetry. In each anion, all the S–P bond distances were equal within error. These distances, and consequently the S–P–S angles, were similar to those observed previously in other S₂PR₂⁻ salts (Table 2). The C–C distances for the linkage between the two aromatic rings were 1.468(4) and 1.476(3) Å in S₂P(C₁₂H₈)⁻ and S₂P(tBu₂C₁₂H₆)⁻, respectively. These values were consistent with the presence of a C(sp²)–C(sp²) single bond. For comparison, the analogous C(sp²)–C(sp²) single bond length in fluorene is 1.472(3) Å. The geometric constraints imposed by the 5-membered dibenzophosphole ring system decreased the C–P–C angles (∼90°) by approximately 10° in comparison to the unconstrained S₂P(C₆H₅)₂⁻ anion, which had an analogous angle of 103.5(1)° (Table 2). In contrast, the S–P–S angles of 118.53(4) and 119.21(3)° in S₂P(C₁₂H₈)⁻ and S₂P(tBu₂C₁₂H₆)⁻ were essentially equivalent to those observed in other S₂PR₂⁻ anions (Table 2).

NMR analysis of HS₂P(R₂C₁₂H₆) (R = H, tBu) vs. [ZPh₄][S₂P(R₂C₁₂H₆)] (R = H, tBu; Z = As, P)

Two aspects of the ³¹P NMR chemical shifts of the new dithiophosphinic acids were notable. First, in chloroform, the ³¹P NMR chemical shifts of the two biphenylenedithiophosphinic acids were near δ 46, vs. a chemical shift from the untethered HS₂P(C₆H₅)₂⁻ anion, which had an analogous angle of 103.5(1)° (Table 2). In contrast, the S–P–S angles of 118.53(4) and 119.21(3)° in S₂P(C₁₂H₈)⁻ and S₂P(tBu₂C₁₂H₆)⁻ were essentially equivalent to those observed in other S₂PR₂⁻ anions (Table 2).

Syntheses and structure of actinide dithiophosphinates

An issue relevant to applications in separations is how the tethering of the aryl rings influences the coordination chem-
istry of dithiophosphinates with actinide elements in comparison to their untethered analogues. However, relatively few actinide compounds have been isolated with untethered diaryldithiophosphinates. To our knowledge, besides some uranyl species,\textsuperscript{33} only Th[S₂P(C₆H₅)₂]\textsuperscript{4},\textsuperscript{34,35} Th[S₂P(o-MeOC₆H₄)₂]\textsuperscript{4} and U[S₂P(o-MeOC₆H₄)₂]\textsuperscript{4}\textsuperscript{–}\textsuperscript{36} as well as some actinide diaryldiselenophosphinates\textsuperscript{37}–\textsuperscript{39} have been described.

Accordingly, we turned our efforts to the investigation of uranium, neptunium, and plutonium complexes that contained the diphenyldithiophosphinate anion, \(\text{S}_2\text{P(C}_6\text{H}_5\text{)}_2\)\textsuperscript{1−}, as a prelude to corresponding studies of the 2,2′-biphenylenephosphinate anion, \(\text{S}_2\text{P(R}_2\text{C}_{12}\text{H}_6\text{)}_2\)\textsuperscript{1−}.

The homoleptic coordination complexes tetrakis(diphenyldithiophosphinato)uranium(IV) and -neptunium(IV) were prepared as shown in eqn (7) and (8) by methods analogous to those used for \(\text{Ln[S}_2\text{PR}_2\text{]}_4\)\textsuperscript{1−},\textsuperscript{38,39} \(\text{An[S}_2\text{PR}_2\text{]}_4\)\textsuperscript{14,36} and \(\text{M[S}_2\text{PR}_2\text{]}_4\)\textsuperscript{14,37} species. Thus, potassium diphenyldithiophosphinato (prepared by deprotonation of the dithiophosphinic acid with potassium hexamethyldisilazide in toluene) reacted with \(\text{UCl}_4\) to afford green needles of \(\text{U[S}_2\text{P(C}_6\text{H}_5\text{)}_2\text{]}_4\) and with \([\text{PPH}_4\text{]}_2\text{[NPcI}_4\text{]}\) or \(\text{NPcI}_4\text{(DME)}_2\) to afford red blocks of \(\text{NP[S}_2\text{P(C}_6\text{H}_5\text{)}_2\text{]}_4\). Crystals suitable for X-ray diffraction studies were obtained by vapor diffusion of \(\text{Et}_2\text{O}\) into concentrated THF solutions. The uranium compound could also be prepared from trivalent uranium starting materials. Thus, treatment of \(\text{U[NSiMe}_3\text{]}_3\) with \(\text{HS}_2\text{P(C}_6\text{H}_5\text{)}_2\) afforded the tetravalent \(\text{UIV[S}_2\text{P(C}_6\text{H}_5\text{)}_2\text{]}_4\) oxidation product in modest yield (64%). The identity of the reduced partner in this redox reaction was not determined. UV-vis, ¹H NMR, and ³¹P NMR spectroscopy was used to characterize the uranium and neptunium compounds (see the Experimental section and the ESI†). The uranium compounds were also characterized by IR-spectroscopy and elemental analysis, but radiological hazards prohibited the use of these techniques with the neptunium compounds.

Our attempts to synthesize the Pu⁴⁺ analogue by a similar means were unsuccessful. Reactions between \([\text{Ph}_4\text{P}]_2\text{[PuCl}_6\text{]}\) and \(\text{HS}_2\text{P(C}_6\text{H}_5\text{)}_2\) or \(\text{KS}_2\text{P(C}_6\text{H}_5\text{)}_2\) generated a mixture of products from which we postulated a transient Pu⁢III species based on UV-vis spectroscopy. However, upon treatment of the trivalent plutonium complex \(\text{PuI}_3\text{(NC}_5\text{H}_5\text{)}_4\)\textsuperscript{40,41} with \(\text{NaS}_2\text{P(C}_6\text{H}_5\text{)}_2\), a few crystals of the neutral bis(pyridine) adduct \(\text{Pu[S}_2\text{P(C}_6\text{H}_5\text{)}_2\text{]}_3\text{(NC}_5\text{H}_5\text{)}_2\) were obtained (eqn (9)).

The above results guided our studies of actinide coordination chemistry with the new 2,2′-biphenylenedithiophosphinate anions. Owing to the relatively poor solubility of \(\text{HS}_2\text{P(C}_6\text{H}_8\text{)}\) in organic solvents, we chose to focus our efforts on exploring the reactivity of the tert-butyl derivative \(\text{HS}_2\text{P(}’\text{Bu}_2\text{C}_12\text{H}_8\text{)}\). Thus, the reaction of \(\text{UCl}_4\) or \(\text{NPcI}_4\text{(DME)}_2\) with

<table>
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<tr>
<th>Compound</th>
<th>S-P (Å)</th>
<th>P-C (Å)</th>
<th>S-P-S (°)</th>
<th>C-P-C (°)</th>
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<tr>
<td>([\text{PPH}_4\text{]}_2\text{[S}_2\text{P(C}_6\text{H}_5\text{)}_2\text{]}_4)</td>
<td>1.977 ± 0.002</td>
<td>1.821 ± 0.002</td>
<td>118.53(4)</td>
<td>90.7(1)</td>
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<td>([\text{AsPh}_4\text{]}_2\text{[S}_2\text{P(}’\text{Bu}_2\text{C}_12\text{H}_8\text{)}_2\text{]}_4)</td>
<td>1.980 ± 0.001</td>
<td>1.820 ± 0.003</td>
<td>119.21(3)</td>
<td>90.75(8)</td>
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<tr>
<td>([\text{PPH}_4\text{]}_2\text{[S}_2\text{P(C}_6\text{H}_5\text{)}_2\text{]}_4)</td>
<td>1.977 ± 0.001</td>
<td>1.832 ± 0.001</td>
<td>118.13(4)</td>
<td>103.5(1)</td>
</tr>
<tr>
<td>([\text{PPH}_4\text{]}_2\text{[S}_2\text{P(o-MeOC}_6\text{H}_4\text{)}_2\text{]}_4)</td>
<td>1.992 ± 0.004</td>
<td>1.838 ± 0.004</td>
<td>117.25(4)</td>
<td>106.9(1)</td>
</tr>
<tr>
<td>([\text{PPH}_4\text{]}_2\text{[S}_2\text{P(o-MeOC}_6\text{H}_4\text{)}_2\text{]}_4)</td>
<td>1.99 ± 0.01</td>
<td>1.836 ± 0.004</td>
<td>115.65(5)</td>
<td>104.4(1)</td>
</tr>
<tr>
<td>([\text{PPH}_4\text{]}_2\text{[S}_2\text{P(o-CF}_3\text{C}_6\text{H}_4\text{)}_2\text{]}_4)</td>
<td>1.984 ± 0.009</td>
<td>1.860 ± 0.006</td>
<td>116.46(8)</td>
<td>111.0(2)</td>
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* This work.
potassium 4,4’-di-tert-butyl-2,2’-biphenylendithiophosphinate, \(K_S_2P(‘Bu_3C_6H_6)\), in THF afforded the homoleptic compounds \(An[S_2P(Bu_3C_6H_6)_4]\), where \(An = U\) or \(Np\), in yields of 76% and 49%, respectively (eqn (10) and (11)). Green prisms of \(U[S_2P(Bu_3C_6H_6)_4]\) were grown from toluene/THF/hexane and dark red prisms of \(Np[S_2P(‘Bu_3C_6H_6)_4]\) were obtained from toluene/Et_2O/hexane. In view of the complex redox behavior observed for \(Pu^{IV}\) with \(S_2P(‘Bu_3C_6H_6)\), reactions between plutonium and the \(S_2P(‘Bu_3C_6H_6)\) were not pursued.

Structural comparisons of \(An[S_2P(C_6H_5)_2]_4\) and \(An[S_2P(Bu_3C_6H_6)_4]\)

The molecular structures of \(Np[S_2P(C_6H_5)_2]_4\), \(Pu[S_2P(C_6H_5)_2]_4\), \(‘Bu_3C_6H_6)_4\) and \(Np[S_2P(Bu_3C_6H_6)_4]\) deduced from single crystal X-ray diffraction experiments have been provided in Fig. 4–6. Crystallographic details of two additional molecules, namely \(U[S_2P(C_6H_5)_2]_4\) and \(U[S_2P(Bu_3C_6H_6)_4]\), were included in the ESI. The \(An[S_2P(C_6H_5)_2]_4\) complexes were iso- morphous with one another. The \(An[S_2P(Bu_3C_6H_6)_4]\) compounds adopted very similar molecular structures, although they crystallized in different space groups (Table 3). Selected distances and angles for all five compounds are summarized in Table 4.

In each of the \(An[S_2P(C_6H_5)_2]_4\) and \(An[S_2P(Bu_3C_6H_6)_4]\) compounds, the eight sulfur atoms of the four bidentate dithiophosphinate ligands described a distorted \(D_{2d}\) trigonal dodecahedron about the actinide center (Fig. 7). Hence, the phosphorus atoms were arranged in the second shell as a flattened tetrahedron. Similarly, for \(Pu[S_2P(C_6H_5)_2]_4[NC_5H_5]_2\), the six sulfur and two nitrogen atoms attached to the plutonium center also described a distorted trigonal dodecahedron around the central \(Pu^{III}\) ion. Within this polyhedron, the pyridine ligands occupied the "outer" sites of one of the two inter-penetrating trapezoids.

The metric parameters internal to the \(S_2P(C_6H_5)_2\) ligand in the \(U\), \(Np\), and \(Pu\) complexes were essentially identical (Table 4). Thus, all of the \(P-S\) distances were \(~2.01\) Å, the \(P-C\) distances were \(~1.81\) Å, and the \(C-Caryl\) distances were \(~1.38\) Å. Similarly, the \(S-P\) angles were \(~110^\circ\) and the \(C-P-C\) angles were \(~105^\circ\). As expected, the \(An-S\) distances depended on the identity of the actinide ion, with the average values of \(2.83 \pm 0.03, 2.82 \pm 0.03, \) and \(2.93 \pm 0.02\) Å for \(U^{IV}\), \(Np^{IV}\), and \(Pu^{III}\), respectively, exactly tracking the actinide ionic radius.

For similar reasons, the measured \(S-M-S\) angles of \(70.6^\circ \pm 0.2\) and \(70.8^\circ \pm 0.1\) for \(U^{IV}\) and \(Np^{IV}\) were slightly smaller (68.70 \pm 0.6) for the larger \(Pu^{III}\) ion.

The distances and angles in the \(An[S_2P(Bu_3C_6H_6)_4]\) complexes were very similar to those observed for the \(An[S_2P(C_6H_5)_2]_4\) complexes (Table 4). For example, the \(P-S\) and \(P-C\) distances were again \(~2.01\) and \(~1.80\) Å, and the \(S-P-S\) and \(S-M-S\) angles were \(~109^\circ\) and \(~70^\circ\). The average \(An-S\) distance of \(2.85 \pm 0.02\) for \(U\) and \(2.83 \pm 0.01\) Å for \(Np\) were also essentially identical with those seen in their \(S_2P(C_6H_5)_2\) analogs. The major difference between the \(An[S_2P(Bu_3C_6H_6)_4]\) and \(An[S_2P(C_6H_5)_2]_4\) structures was the \(C-P-C\) angle. For example, instead of the \(~105^\circ\) value seen for the \(S_2P(C_6H_5)_2\) complexes, this angle was reduced to \(~92^\circ\) in the \(An[S_2P(Bu_3C_6H_6)_4]\) complexes. These observations can be rationalized by the geometric constraints imposed by the 5-membered \(PC_4\) ring.

Concluding remarks

We have described the synthesis of the first \(2,2’\)-biphenylene-dithiophosphinic acids, \(HS_2P(R_2C_6H_5)\), where \(R = H\) or \(‘Bu\). These air and moisture stable salts are chemical relatives of the well-known class of diaryldithiophosphinates, some of
which are able to extract actinides from lanthanide/actinide mixtures. The biphenylenedithiophosphinates differ from other diaryldithiophosphinates in that their aryl rings are tied together by means of a C–C single bond to form a planar 5-membered PC₄ phosphole ring. These new compounds were prepared in multigram quantities, in moderate yield, and in high purity by what was essentially a `one-pot' procedure. Briefly, the synthetic method involved four basic steps: (1st) generation of a biaryl-dianion, (2nd) addition of phosphorus trichloride to form a 5-halo-5⁵H-dibenzo[b,d]phosphole, (3rd) oxidation of the phosphorus atom with elemental sulfur to provide a thiophosphinyl halide, and (4th) nucleophilic addition of sodium hydrosulfide followed by acidification to afford HS₂P(ıtBu₂C₁₂H₆). These dithiophosphinic acids were readily deprotonated to the corresponding S₂P(ıtBu₂C₁₂H₆)⁻ anions, which were isolated as salts with tetr phenylpnictonium cations. The biphenylenedithiophosphinate salts represent interesting candidates for electronic structure studies (currently underway).

We also prepared five new actinide dithiophosphinate complexes, namely U[S₂P(ıtBu₂C₁₂H₆)]₄, Np[S₂P(ıtBu₂C₁₂H₆)]₄, U[S₂P(ıtBu₂C₁₂H₆)]₄, Np[S₂P(ıtBu₂C₁₂H₆)]₄, and Pu[S₂P(C₆H₅)₃(ıtBu₂C₁₂H₆)]₂. These new compounds were characterized and their structures determined by X-ray crystallography. Attempts to prepare the plutonium analogue using Pu⁴⁺ starting materials and S₂P(C₆H₅)₃⁻ produced a mixture of products from which we postulated a transient Pu⁴⁺ species based on UV-vis spectroscopy. However, a stable trivalent plutonium compound, Pu[S₂P(C₆H₅)₃][NC₅H₅]₂, was isolated as single crystals from a
reaction between trivalent PuI₃(NC₅H₅)₄ and S₂P(C₆H₅)₂⁻. In contrast, in the presence of diphenyldithiophosphinate, uranium and neptunium preferred the tetravalent oxidation state. These observations were consistent with reduction potentials reported for these elements (eqn (12)-(14)),

\[
\text{U}^{IV} + 1e^- \rightarrow \text{U}^{III}; \quad e = -0.52 \text{ mV} \quad (12)
\]

\[
\text{Np}^{IV} + 1e^- \rightarrow \text{Np}^{III}; \quad e = +0.15 \text{ mV} \quad (13)
\]

\[
\text{Pu}^{IV} + 1e^- \rightarrow \text{Pu}^{III}; \quad e = +1.01 \text{ mV} \quad (14)
\]
Subtle changes in the relative orientation of the aryl groups may be more significant, especially in view of our recent experimental and theoretical results. This research was conducted in a radiological facility with appropriate safeguards for the safe handling and manipulation of these toxic and radioactive materials.

The starting materials UCl₄, PuI₃(py)₄, [PPh₃]₃[NpCl₄], NpCl₄(DME)$_2$, and U[N(SiMe₃)$_2$]$_3$ were prepared by means of literature-reported procedures. All reactions involving Pu and Np were performed inside an MBraun Labmaster 130® glovebox filled with ultra-high purity helium gas atmosphere, and operated at negative pressure relative to the laboratory atmosphere, using anhydrous solvents (Aldrich) that were further dried over 3 or 4 Å molecular sieves.

All other reactions were performed under argon using standard glovebox or Schlenk techniques with rigorous exclusion of air and moisture unless explicitly stated otherwise. The H₂O used during synthetic manipulations was purified to 18.2 MΩ cm$^{-1}$ resistivity using a Thermo-Scientific Barnstead Nanopure Millipore Nanopure water purification system. Reagents for non-transuranic experiments were obtained from Aldrich, with the exception of elemental sulfur and tetraphenylarsonium chloride hydrate (Acros), and were used as received. Toluene, diethyl ether, and $n$-hexane were dried by vacuum distillation from sodium/benzophenone, and degassed by three freeze–pump–thaw cycles before use. Deuterated solvents were used as received and stored over 3 or 4 Å molecular sieves for several days before use.

Experimental section

General experimental considerations

Caution! The $^{238}$U isotope is a low specific-activity (primarily $\alpha$-emitting radionuclide that decays to $\alpha$, $\beta$, and $\gamma$-emitting isotopes. Its use presents hazards to human health. The $^{237}$Np and $^{239}$Pu isotopes are high specific-activity radionuclides and their use presents relatively higher hazards to human health. This research was conducted in a radiological facility with appropriate safeguards for the safe handling and manipulation of these toxic and radioactive materials.

The structural metrics of the actinide dithiophosphinate complexes suggested that the constraints imposed by the dibenzo[\(b,d\)]phosphole ring system in $\text{S}_2\text{P}\{\text{Bu}_2\text{C}_6\text{H}_5\}_3^{-1}$ had few structural consequences, except the expected closing of the C–P–C angle in comparison to the untethered $\text{S}_2\text{P}\{\text{C}_6\text{H}_5\}_3^{-1}$ ligands. The electronic effects may be more significant, especially in view of our recent experimental and theoretical results, which indicated that the polarizability of the dithiophosphinates and their ability to discriminate between lanthanides and actinides is strongly influenced by subtle changes in the relative orientation of the aryl rings. Hence, our current efforts are focused on characterizing the ability of the $2,2'$-biphenylenedithiophosphinates and related compounds to separate the minor actinides (Am, Cm) from the early lanthanides (Nd, Eu). Moreover, we are hopeful that the synthetic methodology described herein will be useful in the design and synthesis of improved extractants relevant to the development of advanced nuclear fuel cycles.

Table 4 Selected average bond distances and average angles for actinide dithiophosphinate complexes. Error bars are given as standard deviations of the mean (at 1σ).

<table>
<thead>
<tr>
<th></th>
<th>(\text{U[S}_2\text{P}{\text{Bu}_2\text{C}_6\text{H}_5}_4\text{]}\text{r}^{-})</th>
<th>(\text{Np[S}_2\text{P}{\text{Bu}_2\text{C}_6\text{H}_5}_4\text{]}\text{r}^{-})</th>
<th>(\text{U[S}_2\text{P}{\text{C}_6\text{H}_5}_2\text{]}\text{r}^{-})</th>
<th>(\text{Np[S}_2\text{P}{\text{C}_6\text{H}_5}_2\text{]}\text{r}^{-})</th>
<th>(\text{Pu[S}_2\text{P}{\text{C}_6\text{H}_5}_2\text{]}_3{\text{NC}_3\text{H}_5}_2\text{]}\text{r}^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–S (Å)</td>
<td>2.85 ± 0.02</td>
<td>2.83 ± 0.01</td>
<td>2.85 ± 0.03</td>
<td>2.82 ± 0.03</td>
<td>2.93 ± 0.02</td>
</tr>
<tr>
<td>M–N (Å)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>2.62 ± 0.01</td>
</tr>
<tr>
<td>P–S (Å)</td>
<td>2.001 ± 0.007</td>
<td>2.003 ± 0.006</td>
<td>2.014 ± 0.006</td>
<td>2.009 ± 0.003</td>
<td>1.997 ± 0.006</td>
</tr>
<tr>
<td>P–C (Å)</td>
<td>1.800 ± 0.007</td>
<td>1.794 ± 0.003</td>
<td>1.814 ± 0.005</td>
<td>1.809 ± 0.003</td>
<td>1.816 ± 0.006</td>
</tr>
<tr>
<td>C–C$_{\text{ether}}$ (Å)</td>
<td>1.477 ± 0.005</td>
<td>1.477 ± 0.003</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>S–P–S (°)</td>
<td>109.4 ± 0.9</td>
<td>109.8 ± 0.1</td>
<td>109.0 ± 0.1</td>
<td>109.0 ± 0.1</td>
<td>111.8 ± 0.6</td>
</tr>
<tr>
<td>C–P–C (°)</td>
<td>92.4 ± 0.2</td>
<td>92.5 ± 0.3</td>
<td>105.2 ± 1.6</td>
<td>105.2 ± 1.3</td>
<td>104.1 ± 0.9</td>
</tr>
<tr>
<td>S–M–S (°)</td>
<td>70.0 ± 0.7</td>
<td>70.8 ± 0.1</td>
<td>70.6 ± 0.2</td>
<td>70.8 ± 0.1</td>
<td>68.7 ± 0.6</td>
</tr>
</tbody>
</table>

Fig. 7 Ball and stick representation of $\text{Np[S}_2\text{P}\{\text{Bu}_2\text{C}_6\text{H}_5\}_4\text{]}_4$ showing the first coordination sphere of sulfur atoms (yellow distorted trigonal dodecahedron) and the second shell of phosphorus atoms (orange flattened tetrahedron) around the central Np ion (purple).
KBr plates. The $^1$H and $^{31}$P NMR spectra were recorded on a Bruker Avance 300 MHz, Bruker Avance 400 MHz, or Varian VXR 500 MHz NMR spectrometer at ambient temperature; radioactive samples were placed inside 5 mm NMR tubes equipped with 4 mm PTFE tube liners. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS ($^1$H) or H$_3$PO$_4$ ($^{31}$P). High-resolution mass spectra were collected by the School of Chemical Sciences Mass Spectrometry Laboratory at the University of Illinois. Electronic absorption spectra were recorded on a Varian Cary 600i UV/vis/NIR spectrophotometer.

Mixture of 5-chloro-5'H-dibenzophosphole and 5-bromo-5'H-dibenzophosphole, XP(C$_{12}$H$_8$) (X = Br, Cl)

This procedure is a modification of a literature-reported recipe. A solution of 2,2'-dibromobiphenyl (2.49 g, 7.98 mmol) in Et$_2$O (50 mL) was cooled to 0 °C and treated dropwise with $^n$BuLi (10.0 mL of a 1.6 M solution in hexanes, 16.0 mmol). The resulting light yellow solution was stirred at 25 °C for 1 h and then cooled to 196 °C with liquid N$_2$. Phosphorus trichloride (5.0 mL, 57.2 mmol) was then added dropwise on top of the frozen mixture. The flask was allowed to warm to 25 °C, and vigorous stirring was commenced as soon as possible. A white precipitate formed, and the mixture was stirred at 25 °C for an additional 15 min. Volatile material (including excess PCl$_3$) was removed under reduced pressure, and the residue was subsequently kept under vacuum at 35 °C for 1 h. The resulting mixture of BrP(C$_{12}$H$_8$) and ClP(C$_{12}$H$_8$) was separated from a light yellow solid by extraction into toluene (2 × 15 mL); the extracts were filtered and combined. The resulting mixture of 5-halo-5'H-dibenzophospholes in toluene was used in subsequent reactions without further purification. $^{31}$P($^1$H) NMR (162 MHz, toluene): δ 68.2 (s, ClP(C$_{12}$H$_8$), Lit.$^{29}$ δ 69.0 (s, ClP(C$_{12}$H$_8$)). The ratio of BrP(C$_{12}$H$_8$) to ClP(C$_{12}$H$_8$) was ca. 2:3 as judged from integration of the $^{31}$P NMR spectrum.

2,2'-Biphenylenedithiophosphinic acid, HS$_2$P(C$_{12}$H$_8$)

To the above mixture of 5-chloro-5'H-dibenzophosphole and 5-bromo-5'H-dibenzophosphole (theoretical yield: 7.98 mmol) in toluene (30 mL) was added elemental sulfur (256 mg, 0.998 mmol reckoned as S$_8$). After the mixture had been heated to reflux for 16 h, the light yellow solution was cooled to 25 °C and the solvent was removed under vacuum. The flask was opened to air and the yellow solid was suspended in a solution of sodium hydrosulfide hydrate (1.47 g, ca. 15.9 mmol NaSH) in water (75 mL). The flask was equipped with a reflux condenser that was vented with a cannula to a 2.5 M NaOH solution (to sequester evolved H$_2$S). The flask was purged with argon, and the mixture was heated to 90 °C for 1 h, during which time most of the solids dissolved. The mixture was allowed to cool to 25 °C and then was filtered open to air using a vacuum filtration apparatus to remove a small amount of tan precipitate. The filtrate was acidified with 2.4 M aqueous HCl (35 mL). The resulting solution was extracted with CH$_2$Cl$_2$ (3 × 25 mL), and the organic extracts were separated from the aqueous solution, combined, and taken to dryness to afford the product as a light beige powder. Crude yield: 1.15 g (58% from 2,2'-dibromobiphenyl). Further purification was carried out by dissolving HS$_2$P(C$_{12}$H$_8$) in MeCN (75 mL) and allowing the solution to evaporate to approximately 20 mL. This procedure provided HS$_2$P(C$_{12}$H$_8$) as pale yellow plates. Crystalline yield: 1.07 g (54% from 2,2'-dibromobiphenyl). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.98 (dddd, J = 12.2, 7.5, 1.3, 0.7 Hz, 2H, 3,5'-CH), 7.79 (dddd, J = 7.7, 3.6, 1.1, 0.7 Hz, 2H, 6,6'-CH), 7.60 (dddd, J = 7.7, 7.5, 1.9, 1.3 Hz, 2H, 5,5'-CH), 7.51 (dddd, J = 7.5, 7.5, 4.3, 1.1 Hz, 2H, 4,4'-CH). $^{31}$P($^1$H) NMR (162 MHz, CDCl$_3$): δ 46.9 [s]. HRMS m/z (EI$^-$): Calcd: 247.9883 [M$^-$/2]; found: 247.9883. IR (cm$^{-1}$): 3066 m, 2959 s, 2925 s, 2854 s, 2330 br m, 1592 w, 1470 m, 1439 s, 1377 m, 1295 w, 1269 w, 1157 w, 1128 m, 1066 m, 841 w, 756 s, 722 s, 658 s, 617 w, 541 m, 520 w, 483 w, 449 m, 413 m.

Tetraphenylphosphonium 2,2'-biphenylenedithiophosphinate, [PPh$_4$][S$_2$P(C$_{12}$H$_8$)]

A solution of HS$_2$P(C$_{12}$H$_8$) (50.0 mg, 0.201 mmol) in aqueous NH$_4$OH (15 mL of a 3.6 M solution, 0.540 mmol) was treated dropwise in air with a solution of tetrphenylphosphonium chloride (120 mg, 0.320 mmol) in water (5 mL). A white precipitate formed immediately. After the mixture had been stirred at 25 °C for 5 min, the precipitate was collected by vacuum filtration and the solid was washed with H$_2$O (3 × 5 mL). The solid was dissolved in a 1:1 mixture of acetone (5 mL) and H$_2$O (5 mL) and the resulting solution was allowed to evaporate slowly in air to approximately 2 mL. The product was isolated as pale yellow needles. Yield: 48.1 mg (41%). Anal. Calcd for C$_{36}$H$_{28}$P$_2$S$_2$: C, 73.7; H, 4.81; P, 10.46; S, 10.93. Found: C, 73.5; H, 4.67; P, 10.46; S, 10.80%. $^1$H NMR (500 MHz, d$_1$-MeCN): δ 7.94–7.88 (m, 4H, Ar–H), 7.77–7.63 (m, 20H, Ar–H), 7.36 (dddd, J = 7.3, 7.2, 1.6, 1.4 Hz, 2H, 5,5'-CH), 7.33 (dddd, J = 7.2, 7.2, 3.4, 1.3 Hz, 2H, 4,4'-CH). $^{31}$P($^1$H) NMR (162 MHz, d$_1$-MeCN): δ 61.1 (s, S$_2$P(C$_{12}$H$_8$)). IR (cm$^{-1}$): 3408 br, 3057 w, 2924 s, 2855 s, 1585 w, 1463 m, 1438 m, 1377 w, 1316 w, 1261 w, 1162 w, 1107 m, 1026 w, 998 w, 759 m, 724 s, 692 m, 656 s.

3,7-Di-tert-butyl-5-chloro-5'H-dibenzo[b,d]phosphole, ClP($^n$Bu$_2$C$_{12}$H$_8$)

To 4,4'-di-tert-butylbiphenyl (10.65 g, 40.0 mmol) in hexane (75 mL) was added $^n$BuLi (50 mL of a 1.6 M solution in hexanes, 80.0 mmol). To the mixture was added KO'Bu (9.78 g, 80.0 mmol) in one portion against a counterflow of argon. The resulting bright magenta mixture was brought to reflux for 20 h, during which time the solution color became deep purple. The solution was cooled to −196 °C with liquid N$_2$, and phosphorus trichloride (20.0 mL, 235 mmol) was added dropwise on top of the frozen mixture. The flask was allowed to warm to 25 °C, and vigorous stirring was commenced as soon as possible. As the mixture warmed, a slight exotherm occurred, and the solution color changed from purple to brown and then yellow, and a white precipitate formed. The solution was transferred by using a filter cannula to a separate
flask, and the solid left behind was washed with hexane (2 × 20 mL). The washings were added to the original filtrate, and the volatile material was removed under vacuum to afford a viscous yellow oil. The oil was dried overnight at 35 °C to 10⁻³ Torr to a yellow solid, which was used without purification in the next step. ³¹P{¹H} NMR (162 MHz, hexane): δ 70.2 (s).

**4,4′-Di-tert-butyl-2,2′-biphenylenedithiophosphinic acid, HS₂P(Bu₂C₁₂H₁₆)**

To a solution of 3,7-di-tert-butyl-5-chloro-5H-dibenzo-1,3,2'-dithiophosphole (theoretical yield: 40 mmol) in toluene (50 mL) was added elemental sulfur (1.28 g, 5.0 mmol reckoned as S₈) against a cold ethanol solution of KN(SiMe₃)₂ (1.31 g, 6.57 mmol) in toluene (20 mL). The washings were added to the original filtrate, and the solid left behind was washed with hexane (2 × 10 mL), and dried under vacuum to afford the product as a white powder. Yield: 1.94 g (82%). ¹H NMR (400 MHz, d₆-acetone): δ 7.77 (dd, J = 11.4, 1.8 Hz, 2H, 3,3′-CH), 7.62 (dd, J = 8.0, 3.2 Hz, 2H, 6,6′-CH), 7.38 (dd, J = 8.0, 1.8, 1.7 Hz, 2H, 5,5′-CH), 1.35 (s, 18H, C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, d₆-acetone): δ 61.6 (s). The microanalytical and IR data suggest the presence of the hydrate K[S₂P(Bu₂C₁₂H₁₆)]·H₂O. Anal. Calcd for C₂₀H₂₆P₂O₅S₂K: C, 57.66; H, 6.29; P, 7.43; S, 15.39; K, 9.38. Found: C, 58.36; H, 6.07; P, 7.08; S, 14.51; K, 9.09%. IR (cm⁻¹): 3387 br, 2929 s, 2855 s, 2348 m br, 1923 w, 1809 w, 1779 w, 1689 w, 1661 w, 1599 w, 1572 w, 1462 s br, 1405 w, 1378 w, 1363 m, 1302 w, 1277 m, 1255 m, 1156 m, 1156 m, 1110 m, 1084 w, 1061 w, 1061 w, 1061 m, 874 w, 829 s, 794 w, 733 s, 723 s, 671 s, 603 m, 535 s.

**Potassium diphenyldithiophosphinate**

To a solution of KN(SiMe₃)₂ (392 mg, 1.97 mmol) in toluene (10 mL) was added a solution of HS₂P(C₆H₅)₂ (489 mg, 1.95 mmol) in toluene (5 mL). After 24 h, the mixture was centrifuged and the white solid was collected by filtration and washed with hexane (3 × 10 mL) and hexanes (2 × 10 mL), and dried under vacuum to afford the product as a white powder. Yield: 1.94 g (82%). ¹H NMR (400 MHz, d₆-acetone): δ 7.97 (dd, J = 13.4, 1.7 Hz, 2H, 3,3′-CH), 7.67 (dd, J = 8.1, 4.2 Hz, 2H, 6,6′-CH), 7.61 (dd, J = 8.1, 1.7, 1.7 Hz, 2H, 5,5′-CH), 1.40 (s, 18H, C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, d₆-acetone): δ 46.4 (s). HRMS m/z [ESI⁺]. Calcd: 361.1214 [M + H⁺]. Found: 361.1215 [M + H⁺].

**Tetraphenylarsonium 4,4′-di-tert-butyl-2,2′-biphenylenedithiophosphinate, [AsPh₄][S₂P(Bu₂C₁₂H₁₆)]**

This compound was synthesized by treating a solution of HS₂P(Bu₂C₁₂H₁₆) (100.0 mg, 0.277 mmol) in aqueous NH₄OH (20.0 mL, 3.6 M) with a solution of tetraphenylarsine (0.58 mmol) in toluene (5 mL). The mixture was stirred at 25 °C for 14 h, during which time the solution color became orange and a gummy white solid precipitated. The solution was separated from the solid by vacuum filtration in air, and the filtrate was washed with hexanes (3 × 25 mL). The solution was transferred to a 250 Erlenmeyer flask, acidified with 2.4 M aqueous HCl (25 mL), and allowed to stir in air for 30 min. The light yellow precipitate that formed was collected by vacuum filtration and dissolved in CH₂Cl₂ (40 mL). The resulting solution was dried over MgSO₄, and taken to dryness under vacuum to afford a sticky yellow solid, which was triturated with absolute ethanol (60 mL). After the ethanol was removed, the solution was treated with a solution of sodium hydroxide (7.47 g, 0.1 molar concentration) in H₂O : EtOH (1 : 2 ratio with a total volume of 60 mL). The flask was purged with argon and vented with a cannula to a 2.5 M aq. NaOH solution to sequester evolved H₂S. The mixture was stirred at 25 °C for 14 h, during which time the solution color became orange and a gummy white solid precipitated. The solution was separated from the solid by vacuum filtration in air, and the filtrate was washed with hexanes (3 × 25 mL). The solution was transferred to a 250 Erlenmeyer flask, acidified with 2.4 M aqueous HCl (25 mL), and allowed to stir in air for 30 min. The light yellow precipitate that formed was collected by vacuum filtration and dissolved in CH₂Cl₂ (40 mL). The resulting solution was dried over MgSO₄, and taken to dryness under vacuum to afford the product as a free-flowing, pale yellow powder. Yield: 7.48 g (52% from 4,4′-di-tert-butylbiphenyl). ¹H NMR (400 MHz, CDCl₃): δ 7.97 (dd, J = 13.4, 1.7 Hz, 2H, 3,3′-CH), 7.67 (dd, J = 8.1, 4.2 Hz, 2H, 6,6′-CH), 7.61 (dd, J = 8.1, 1.7, 1.7 Hz, 2H, 5,5′-CH), 1.40 (s, 18H, C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 46.4 (s). UV/vis/NIR λmax nm (THF). UV/vis/NIR in THF solution (λmax nm) 3387 br, 2919 s, 2856 s, 1614 w, 1459 s, 1396 w, 1363 m, 1212 m, 1202 w, 1156 m, 1111 m, 1081 w, 1059 w, 823 m, 794 w, 727 s, 647 s, 580 m.

**Tetrakis[diphenyldithiophosphinato]uranium(IV), [U(S₂P(C₆H₅)₂)₄]**

Method A. To a solution of U[N(SiMe₃)₂]₃ (90.0 mg, 0.125 mmol) in THF (7 mL) was added solid HS₂P(C₆H₅)₂ (94.0 mg, 0.376 mmol). The resulting mixture was stirred at ambient temperature for 3 days, and the green solution was filtered through a glass fiber filter circle. Hexanes were added to the green filtrate until a precipitate began to form. The mixture was stored at −35 °C for 2 h. The precipitate was collected on a frit by vacuum filtration, washed with hexanes (3 × 10 mL) and hexanes (2 × 10 mL), and dried under vacuum to afford the product as a white powder (460 mg; 82% yield), and used as KS₂P(C₆H₅)₂ for subsequent reactions.
The toluene was removed under vacuum (10⁻³ Torr), and the resulting residue was dissolved in toluene (~5 mL). A small amount of an insoluble white precipitate was again separated by centrifugation. The toluene was taken to dryness under vacuum to 1.5 mL and Et₂O was vapor diffused at ambient temperature. 

Method B. In an argon filled glovebox, to a solution of UCl₄ (38.4 mg, 0.101 mmol) in THF (10 mL) was added a solution of KS₂P(C₆H₅)₂ (29.8 mg, 0.103 mmol) in THF (5 mL). The initially green color changed to yellow. After the mixture had been stirred for 24 h, it was centrifuged and the solution was separated from a white solid by filtration. The filtrate was taken to dryness under vacuum (10⁻³ Torr), and the resulting residue was dissolved in toluene (~5 mL). A small amount of an insoluble white precipitate was again separated by centrifugation. The toluene was removed under vacuum (10⁻³ Torr) and the resulting lime-colored solid was dissolved in a minimal amount of hot THF. The solution was slowly cooled to ~25 °C. After 24 h, toluene was layered on the THF solution. After 1 week, the lime-colored crystals were collected. Yield: 35.0 mg (28%).

Tetrakis(diphenyldithiophosphinato)neptunium(n), Np[S₂P(C₆H₅)₂]₄

Method A. To [PPh₄]₂[NpCl₆] (6.6 mg, 0.006 mmol) was added a solution of KS₂P(C₆H₅)₂ (6.7 mg, 0.023 mmol) in THF (3 mL). The mixture was centrifuged and the yellow solution was filtered through a glass fiber filter circle. The deep red filtrate was stored at 35 °C. After 2 days, red block-like crystals were collected. Yield: 35.0 mg (28%).

Method B. To solid [PPh₄]₂[NpCl₆] (20.1 mg, 0.018 mmol) was added a solution of NaS₂P(C₆H₅)₂ formed by treating HS₂P(C₆H₅)₂ (16.5 mg, 0.066 mmol) with Na[N(SiMe₃)₂] (12.2 mg, 0.067 mmol) in THF (2 mL). The mixture, which quickly turned green, was stirred at ambient temperature for 6 h. The green-brown solution was taken to dryness under vacuum and the resulting green residue was dissolved in toluene (0.75 mL). The solution was filtered through a glass fiber filter circle to afford an intensely colored filtrate, into which Et₂O was slowly vapor diffused at ~35 °C. After one week, a few green needles of Pu[S₂P(C₆H₅)₂]₃(NC₅H₅) were separated by centrifugation and the resulting green residue was dissolved in toluene suitable for X-ray diffraction. 

Tetrakis(4,4'-di-tert-butyl-2,2'-biphenylenedithiophosphinato)-uranium(n), U[S₂P₄(Bu₂C₆H₅)₁₂]₄

To a solution of uranium tetrachloride (12.5 mg, 0.033 mmol) in THF (3 mL) was added a solution of potassium 4,4'-di-tert-butyl-2,2'-biphenylenedithiophosphinate (52.6 mg, 0.132 mmol) in THF (5 mL). The mixture, which became turbid, was stirred at 25 °C for 22 h. The solvent was removed under reduced pressure and to the resulting residue was added toluene (2 × 5 mL). The mixture was centrifuged and the yellow solution was filtered away from a white solid. The filtrate was taken to dryness under vacuum to afford the product as a green-yellow solid. Yield: 42.3 mg (76%). Anal. Calc'd for C₉₀H₅₈PS₄U: C, 57.33; H, 5.77; P, 7.39; S, 15.30; U, 14.20. Found: C, 57.83; H, 5.92%.

Tetrakis(4,4'-di-tert-butyl-2,2'-biphenylenedithiophosphinato)neptunium(n), Np[S₂P₄(Bu₂C₆H₅)₁₂]₄

To a solution of PuI₃(NC₅H₅)₄ (20.6 mg, 0.022 mmol) in THF (2 mL) was added a solution of NaS₂P(C₆H₅)₂ formed by treating H₅S₂P(C₆H₅)₂ (16.5 mg, 0.066 mmol) with Na[N(SiMe₃)₂] (12.2 mg, 0.067 mmol) in THF (2 mL). The mixture, which quickly turned green, was stirred at ambient temperature for 6 h. The green-brown solution was taken to dryness under vacuum and the resulting green residue was dissolved in toluene (0.75 mL). The solution was filtered through a glass fiber filter circle to afford an intensely colored filtrate, into which Et₂O was slowly vapor diffused at ~35 °C. After one week, a few green needles of Pu[S₂P(C₆H₅)₂]₃(NC₅H₅)₂-toluene formed that were suitable for single-crystal X-ray diffraction. 

Pure bulk product could not be obtained, possibly because the reaction generated several species: the ³¹P NMR spectrum of the reaction solution contained multiple broad resonances due to paramagnetic compounds.
The filtrate was concentrated under vacuum to 2.5 mL, layered with Et₂O (2.5 mL) and hexanes (13 mL), and stored at −35 °C. After eight days the red microcrystals were collected, washed with hexanes (7 mL), and dried under vacuum. Yield: 6.1 mg (9%). The unextracted red solid was dissolved in THF (4 mL) with heating at 40 °C, and the resulting solution was filtered through Celite supported on a glass fiber filter circle (to remove some undissolved white solid, presumably KCl). The deep red filtrate was layered with hexanes (6 mL) and stored at −35 °C. After three days, the red crystals that had deposited were collected, washed with hexanes (7 mL), and dried under vacuum. Yield: 33.1 mg (49%). The total combined crystalline yield of the two crops was 58%. ¹¹H NMR (400 MHz, CD₂Cl₂): δ 8.2 (s, 8H, 3,3′-CH), 7.5 (d, J = 7.3 Hz, 8H, 6,6′-CH), 7.4 (d, J = 8.2 Hz, 8H, 5,5′-CH), 1.4 (s, 72H, –C(CH₃)₃). ³¹P[¹¹H] NMR (121 MHz, CD₂Cl₂): δ −715 (br s). UV/vis/NIR (THF; λ_max, nm): 480, 693, 714 sh, 755, 778, 814, 852, 893, 919, 971, 1025, 1284, 1322. Single crystals suitable for X-ray diffraction were obtained by adding five drops of THF to a toluene solution of the product, then layering with hexanes (5 mL) followed by storage at −35 °C. After 6 days several large, deep-red, block shaped crystals of Np[S₂P[(Bu₂C₁₂H₃O)]₄toulene] had formed.

Crystallographic details

Single crystals of the non-transuranic containing compounds were mounted in a nylon cryoloop with Paratone-N oil under argon gas flow. To ensure safe handling during the diffraction studies, crystals containing the transuranic elements Np and Pu were prepared for analyses with three appropriate layers of containment prior to single crystal X-ray diffraction studies by the following modifications to published procedures.⁴¹,⁴⁶,⁴⁸,⁴⁹ Each transuranic crystal was coated in Paratone-N oil and mounted inside a 0.5 mm diameter quartz capillary, the ends were sealed with capillary wax, and the exterior of the capillary was coated with acrylic (‘Hard as Nails’ nail polish) dissolved in ethyl acetate. The data were collected on a Bruker D8 diffractometer equipped with an APEX II charge-coupled-device (CCD) detector. The crystal was cooled to 120(1) K by means of an American Cryo Industries low temperature device. Data for Np[S₂P[(Bu₂C₁₂H₃O)]₄toulene] were collected on a Bruker D8 Quest with a CMOS detector, and an Oxford cryostream was used to cool the crystal to 100 K. Both instruments were equipped with a graphite monochromatized MoKα X-ray source (λ = 0.71073 Å). A hemisphere of data was collected using ω scans, with 10–30 second frame exposures and 0.5° frame widths. Data collection, cell indexing, integration, and absorption corrections were performed using standard Bruker software, with details reported in the ESI.† Decay of reflection intensity was not observed as monitored via analysis of redundant frames. The structure was solved by means of direct methods and difference Fourier techniques. All hydrogen atom positions were idealized. The final refinement model included anisotropic temperature factors for all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXL and Mercury.⁵⁰

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