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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 diaryldithiophosphinic 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 tetraphenylpnictonium cations (ZPh₄¹⁺; Z = P or As). Coordination chemistry between [S₂P(^tBu₂C₁₂H₆)]¹⁻ and [S₂P(C₆H₅)₂]¹⁻ with U, Np, and Pu was comparatively investigated. The results showed that dithiophosphinate complexes of U^{IV} and Np^{IV} were redox stable relative to those of U^{III}, whereas reactions involving Pu^{IV} gave intractable material. For instance, reactions involving U^{IV} and Np^{IV} generated An[S₂P(^tBu₂C₁₂H₆)]₄ and An[S₂P(C₆H₅)₂]₄ whereas reactions between Pu^{IV} and [S₂P(C₆H₅)₂]¹⁻ generated a mixture of products from which we postulated a transient Pu^{III} 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)₂]¹⁻ and the trivalent PuI₃(NC₅H₅)₄ starting material. Attempts to synthesize analogous trivalent compounds with U^{III} provided the tetravalent U[S₂P(C₆H₅)₂]₄ oxidation product.

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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 (transmuted) to short-lived isotopes in fast breeder reactors. Partitioning and trans-

mutation 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,^{3,10-17} 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 (SF_{Am/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

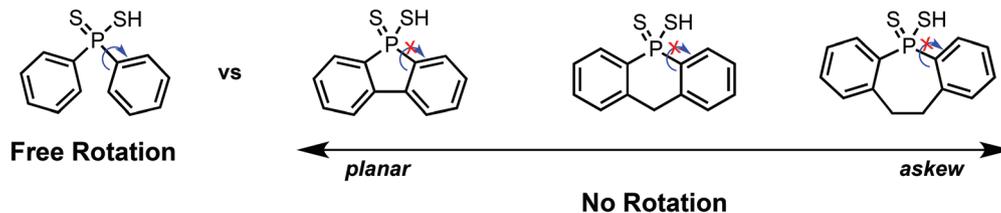
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Scheme 1 Tethering of the aryl rings ensures that they are unable to rotate freely about the P–C_{ipso} bond. The size of the central heterocycle can be used to further manipulate orbital mixing between the aryl groups and the PS₂^{1–} core.

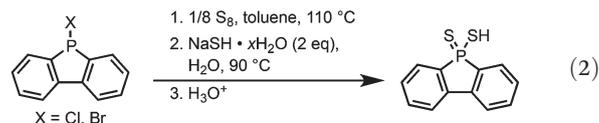
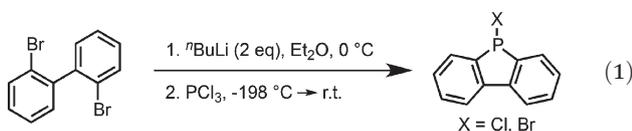
vs. the more ionic Eu–S₂PR₂ interactions.^{18,26} Recent structural, spectroscopic, and theoretical studies of a series of S₂PR₂^{1–} anions (R = Me, C₆H₅, *p*-CF₃C₆H₄, *m*-CF₃C₆H₄, *o*-CF₃C₆H₄, *o*-MeC₆H₄, *o*-MeOC₆H₄) revealed that the Am/Eu separation factors were correlated with the extent and nature of π-mixing between the aryl groups and the PS₂^{1–} core of the dithiophosphinate extractant.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 entatic state²⁸ 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 dibenzophosphole ring. These efforts include the preparation of the 2,2'-biphenylenedithiophosphinic acids, HS₂P(R₂C₁₂H₆) (R = H or ^tBu), and their conjugate bases, S₂P(R₂C₁₂H₆)^{1–}, which were isolated as salts with tetraphenylpnictonium cations (ZPh₄¹⁺; 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, S₂P(C₆H₅)₂^{1–}. These reactivity studies provided a useful platform for evaluating how actinide coordination chemistry with dithiophosphinates was (or was not) affected by the tethering of the aryl rings. Moreover, they highlighted the different stabilities of the An^{III} and An^{IV} oxidation states of uranium, neptunium, and plutonium in the presence of dithiophosphinate salts.

Results and discussion

Syntheses of HS₂P(R₂C₁₂H₆) (R = H, ^tBu)

The compound 2,2'-biphenylenedithiophosphinic acid, HS₂P(C₁₂H₈), was prepared as described in eqn (1) and (2).



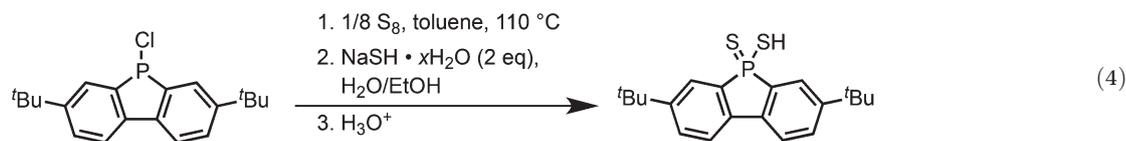
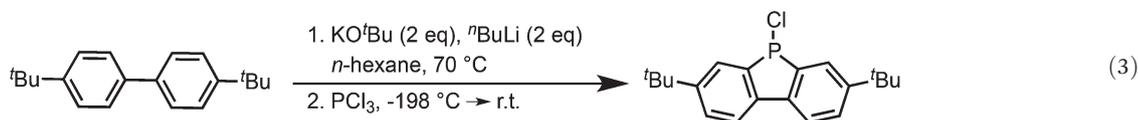
The synthetic procedure began with treating the commercially available 2,2'-dibromobiphenyl, Br₂C₁₂H₈, with two equivalents of *n*-butyllithium to generate the known 2,2'-dilithiobiphenyl compound, Li₂(C₁₂H₈).²⁹ This organolithium reagent has been reported to react with phosphorus trichloride to generate 5-chloro-5*H*-dibenzo[*b,d*]phosphole in good yield.²⁹ In our hands, this reaction afforded a second product that was characterized by ³¹P NMR spectroscopy as 5-bromo-5*H*-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.¹⁹ It was not necessary to separate the 5-chloro-5*H*-phosphole from the 5-bromo-5*H*-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.^{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·*x*H₂O) and aqueous workup cleanly provided the desired 2,2'-biphenylenedithiophosphinic acid, HS₂P(C₁₂H₈), in 54% overall yield from Br₂C₁₂H₈.

This 'one-pot' sulfurization method had 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 H₂S) to the corresponding anhydrosulfide. 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.

Similar methodology was used to prepare the di-*tert*-butyl substituted derivative, 4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphinic acid, $\text{HS}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)$, as illustrated in eqn (3) and (4).

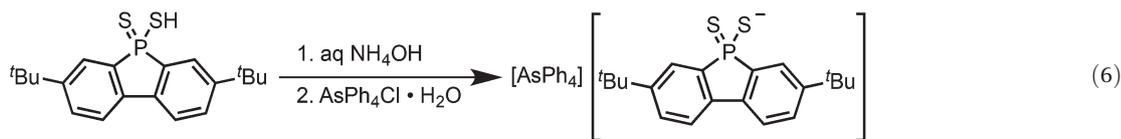
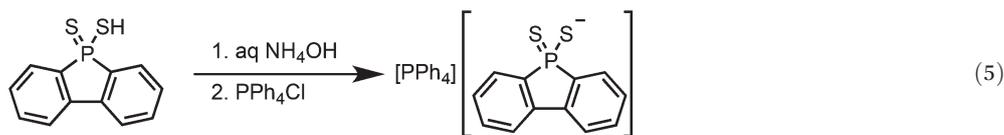
logue, $\text{HS}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)$, readily dissolved in all of these solvents except *n*-hexane. We anticipate that the more soluble acid, $\text{HS}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)$, is better suited for use as an actinide ligand and as an extractant in liquid/liquid separation schemes.



The synthesis relied on previous work that had established that 4,4'-di-*tert*-butylbiphenyl, $\text{Bu}_2\text{C}_{12}\text{H}_8$, could be deprotonated at the 2 and 2' positions with Schlosser's base, $n\text{BuLi}/\text{KO}^t\text{Bu}$.³¹ 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, $\text{ClP}(\text{Bu}_2\text{C}_{12}\text{H}_6)$. Treatment of the chlorophosphole with elemental sulfur and sodium hydrosulfide hydrate (as discussed above)

Syntheses and structures of $[\text{ZPh}_4][\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)]$ ($\text{R} = \text{H}, ^t\text{Bu}$; $\text{Z} = \text{As}, \text{P}$)

The $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$ and $\text{HS}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)$ acids were readily deprotonated with aqueous NH_4OH in air as shown in eqn (5) and (6). Subsequent addition of tetraphenylpnictonium chloride (ZPh_4Cl , $\text{Z} = \text{P}$ or As) provided the $[\text{ZPh}_4][\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)]$ salts in reasonable crystalline yields ranging from 41 to 45%.



afforded the 4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphinic acid, $\text{HS}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)$, 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, $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$, was only moderately ($<20 \text{ mg mL}^{-1}$) soluble in halogenated solvents (chloroform and dichloromethane) and was essentially insoluble in acetonitrile, toluene, tetrahydrofuran, diethyl ether, and *n*-hexane. In contrast, the substituted ana-

Single crystals of $[\text{PPh}_4][\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)]$ and $[\text{AsPh}_4][\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]$ suitable for X-ray diffraction studies were grown by slow evaporation of acetone/water solutions. We note that single crystals of $[\text{PPh}_4][\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]$ were also obtained, but the disorder associated with the $\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)^{1-}$ anions prevented the generation of a meaningful structural model. The structural metrics for $[\text{PPh}_4][\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)]$ and $[\text{AsPh}_4][\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]$ 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

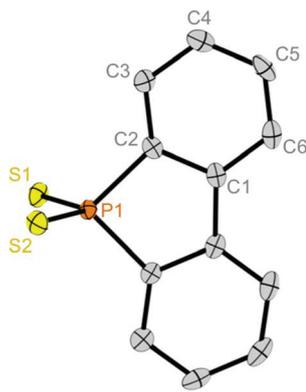


Fig. 1 Molecular structure of the anion in $[\text{PPh}_4][\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)]$. Thermal ellipsoids show the 50% probability density surfaces. The PPh_4^{1+} cation and hydrogen atoms have been omitted.

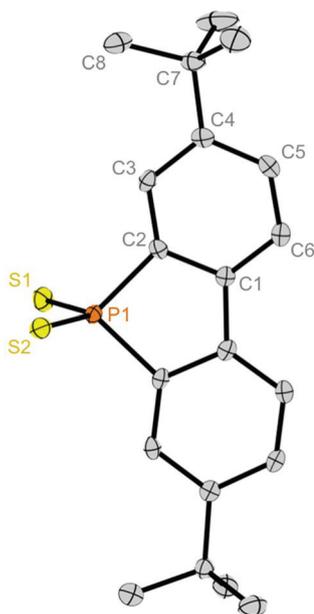


Fig. 2 Molecular structure of the anion in $[\text{AsPh}_4][\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]$. Thermal ellipsoids show the 50% probability density surfaces. The AsPh_4^{1+} cation, solvent molecules, and hydrogen atoms have been omitted.

dibenzophosphole unit. In both $[\text{PPh}_4][\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)]$ and $[\text{AsPh}_4][\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]$, 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 $\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)^{1-}$ anions had a nearly ideal C_{2v} 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 $\text{S}_2\text{PR}_2^{1-}$ salts (Table 2). The C–C distances for the linkage between

Table 1 Crystallographic data for $[\text{PPh}_4][\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)]$ and $[\text{AsPh}_4][\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)] \cdot 0.5$ acetone collected at 120(1) K

	$[\text{PPh}_4][\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)]$	$[\text{AsPh}_4][\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)] \cdot 0.5$ acetone
Formula	$\text{C}_{34}\text{H}_{28}\text{P}_2\text{S}_2$	$\text{C}_{45.5}\text{H}_{47}\text{O}_{0.5}\text{AsPS}_2$
Formula wt (g mol^{-1})	586.69	771.84
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	11.616(4)	12.5652(13)
b (Å)	16.103(5)	13.0602(14)
c (Å)	16.319(5)	14.2301(15)
α (°)	90	110.587(1)
β (°)	109.164(4)	91.766(1)
γ (°)	90	114.432(1)
V (Å ³)	2883.3(16)	1947.3(4)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.351	1.316
μ (mm^{-1})	0.321	1.054
Data/restraints/params	5494/0/361	9192/0/439
Goodness-of-fit on F^2	1.198	1.410
R_1 [$F^2 > 2\sigma(F^2)$]	0.0386	0.0333
wR_2 (all data)	0.0863	0.0627
Largest $\Delta\rho$ (e Å^{-3})	0.364/−0.339	0.575/−0.325

the two aromatic rings were 1.468(4) and 1.476(3) Å in $\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)^{1-}$ and $\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)^{1-}$, respectively. These values were consistent with the presence of a $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ single bond. For comparison, the analogous $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ single bond length in fluorene is 1.472(3) Å.³² The geometric constraints imposed by the 5-membered dibenzophosphole ring system decreased the C–P–C angles ($\sim 90^\circ$) by approximately 10° in comparison to the unconstrained $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$ anion, which had an analogous angle of $103.5(1)^\circ$ (Table 2).²⁷ In contrast, the S–P–S angles of $118.53(4)$ and $119.21(3)^\circ$ in $\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)^{1-}$ and $\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)^{1-}$ were essentially equivalent to those observed in other $\text{S}_2\text{PR}_2^{1-}$ anions (Table 2).

NMR analysis of $\text{HS}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)$ ($\text{R} = \text{H}, \text{tBu}$) vs. $[\text{ZPh}_4][\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)]$ ($\text{R} = \text{H}, \text{tBu}; \text{Z} = \text{As}, \text{P}$)

Two aspects of the ^{31}P NMR chemical shifts of the new dithiophosphinic acids were notable. First, in chloroform, the ^{31}P NMR chemical shifts of the two biphenylenedithiophosphinic acids were near δ 46, vs. a chemical shift from the untethered $\text{HS}_2\text{P}(\text{C}_6\text{H}_5)_2$ analogue at δ 56. This comparison shows that tethering of the two aryl rings shielded the ^{31}P nucleus by 10 ppm. Second, the change in chemical shift between the free acid HS_2PR_2 in chloroform and the conjugate base $\text{S}_2\text{PR}_2^{1-}$ in acetonitrile was 15 ppm for the two biphenylenedithiophosphinic acids, but only 5 to 9 ppm for a series of untethered diaryldithiophosphinic acids (Fig. 3).²⁷ Both of these differences may reflect changes in the electronic structure that result from the coplanarity of the aryl rings and the phosphorus atom.

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-

Table 2 Selected bond distances and angles for [PPh₄][S₂P(C₁₂H₈)], [AsPh₄][S₂P(^tBu₂C₁₂H₆)], and other diaryldithiophosphinates. Error bars are given as standard deviations of the mean (at 1σ)

Cmpd	S–P (Å)	P–C (Å)	S–P–S (°)	C–P–C (°)
[PPh ₄][S ₂ P(C ₁₂ H ₈)] ^a	1.977 ± 0.002	1.821 ± 0.002	118.53(4)	90.7(1)
[AsPh ₄][S ₂ P(^t Bu ₂ C ₁₂ H ₆)] ^a	1.980 ± 0.001	1.820 ± 0.003	119.21(3)	90.75(8)
[PPh ₄][S ₂ P(C ₆ H ₅) ₂] ²⁷	1.977 ± 0.001	1.832 ± 0.001	118.13(4)	103.5(1)
[PPh ₄][S ₂ P(<i>o</i> -MeC ₆ H ₄) ₂] ²⁷	1.992 ± 0.004	1.838 ± 0.004	117.25(4)	106.9(1)
[PPh ₄][S ₂ P(<i>o</i> -MeOC ₆ H ₄) ₂] ²⁷	1.99 ± 0.01	1.836 ± 0.004	115.65(5)	104.4(1)
[PPh ₄][S ₂ P(<i>o</i> -CF ₃ C ₆ H ₄) ₂] ²⁷	1.984 ± 0.009	1.860 ± 0.006	116.46(8)	111.0(2)

^a This work.

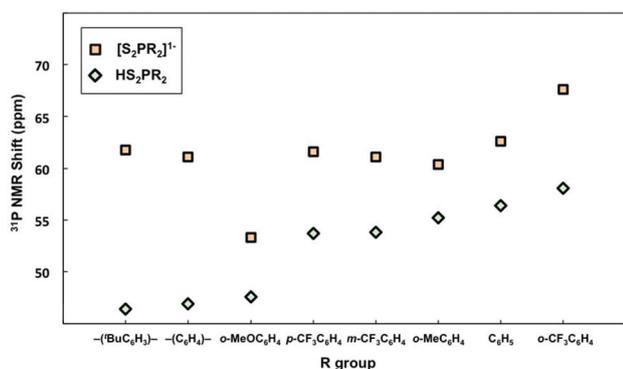


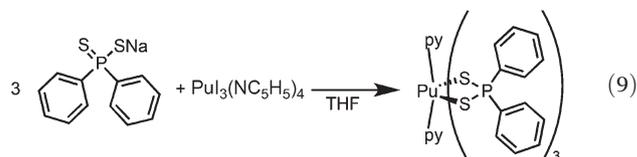
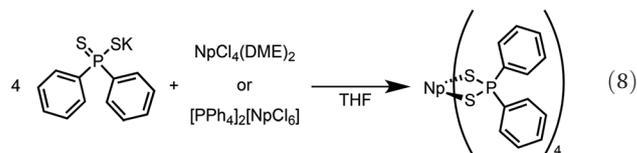
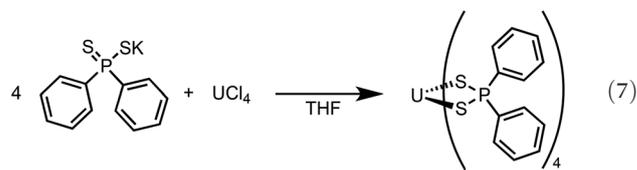
Fig. 3 ³¹P NMR shifts for the HS₂PR₂ and [S₂PR₂]¹⁻ compounds in CDCl₃ and d₃-MeCN, respectively.

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,³³ only Th[S₂P(C₆H₅)₂]₄,^{34,35} Th[S₂P(*p*-MeOC₆H₄)₂]₄,³⁶ and U[S₂P(*p*-MeOC₆H₄)₂]₄³⁶ – as well as some actinide diaryldiselenophosphinates³⁷ – have been described. Accordingly, we turned our efforts to the investigation of uranium, neptunium, and plutonium complexes that contained the diphenyldithiophosphate anion, S₂P(C₆H₅)₂¹⁻, as a prelude to corresponding studies of the 2,2'-biphenylenephosphate anion, S₂P(R₂C₁₂H₆)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 Ln(S₂PR₂)₄¹⁻,^{38,39} An(S₂PR₂)₄,^{34,36} and M(S₂PR₂)₄^{36,37} species. Thus, potassium diphenyldithiophosphate (prepared by deprotonation of the dithiophosphinic acid with potassium hexamethyldisilazide in toluene) reacted with UCl₄ to afford green needles of U[S₂P(C₆H₅)₂]₄ and with [PPh₄]₂[NpCl₆] or NpCl₄(DME)₂ to afford red blocks of Np[S₂P(C₆H₅)₂]₄. Crystals suitable for X-ray diffraction studies were obtained by vapor diffusion of Et₂O into concentrated THF solutions. The uranium compound could also be prepared from trivalent uranium starting materials. Thus, treatment of

U[N(SiMe₃)₂]₃ with HS₂P(C₆H₅)₂ afforded the tetravalent U^{IV}[S₂P(C₆H₅)₂]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.

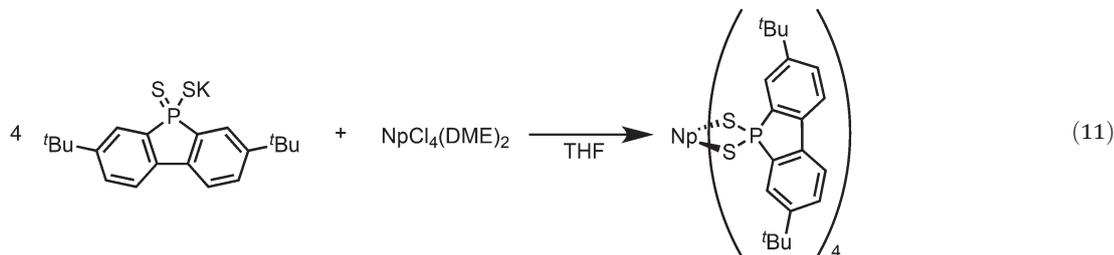
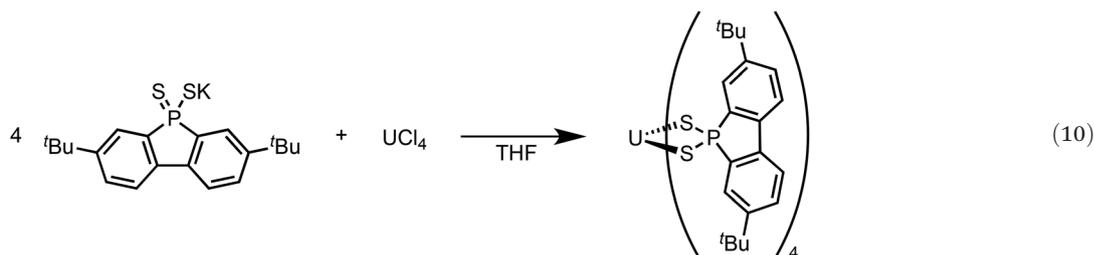
Our attempts to synthesize the Pu^{IV} analogue by a similar means were unsuccessful. Reactions between [Ph₄P]₂[PuCl₆] and HS₂P(C₆H₅)₂ or KS₂P(C₆H₅)₂ generated a mixture of products from which we postulated a transient Pu^{III} species based on UV-vis spectroscopy. However, upon treatment of the trivalent plutonium complex PuI₃(NC₅H₅)₄^{40,41} with NaS₂P(C₆H₅)₂, a few crystals of the neutral bis(pyridine) adduct Pu[S₂P(C₆H₅)₂]₃(NC₅H₅)₂ were obtained (eqn (9)).



The above results guided our studies of actinide coordination chemistry with the new 2,2'-biphenylenedithiophosphate anions. Owing to the relatively poor solubility of HS₂P(C₁₂H₈) in organic solvents, we chose to focus our efforts on exploring the reactivity of the *tert*-butyl derivative HS₂P(^tBu₂C₁₂H₆). Thus, the reaction of UCl₄ or NpCl₄(DME)₂ with

potassium 4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphate, $\text{KS}_2\text{P}(\text{C}_6\text{H}_5)_2$, in THF afforded the homoleptic compounds $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ where $\text{An} = \text{U}$ or Np , in yields of 76% and 49%, respectively (eqn (10) and (11)). Green prisms of $\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ were grown from toluene/THF/hexane and dark red prisms of $\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ were obtained from toluene/Et₂O/hexane. In view of the complex redox behavior observed for Pu^{IV} with $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$, reactions between plutonium and the $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$ were not pursued.

The metric parameters internal to the $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$ ligand in the U, Np, and Pu complexes were essentially identical (Table 4). Thus, all of the P–S distances were $\sim 2.01 \text{ \AA}$, the P–C distances were $\sim 1.81 \text{ \AA}$, and the C–C_{aryl} distances were $\sim 1.38 \text{ \AA}$. Similarly, the S–P–S angles were $\sim 110^\circ$ and the C–P–C angles were $\sim 105^\circ$. As expected, the An–S distances depended on the identity of the actinide ion, with the average values of 2.85 ± 0.03 , 2.82 ± 0.03 , and $2.93 \pm 0.02 \text{ \AA}$ for U^{IV} , Np^{IV} , and Pu^{III} , respectively, exactly tracking the actinide ionic radius.



Structural comparisons of $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ and $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$

The molecular structures of $\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$, $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_5\text{H}_5)_2$ and $\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ deduced from single crystal X-ray diffraction experiments have been provided in Fig. 4–6. Crystallographic details of two additional molecules, namely $\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ and $\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$, were included in the ESI.† The $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ complexes were isomorphous with one another. The $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ 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 $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ and $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ compounds, the eight sulfur atoms of the four bidentate dithiophosphate 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 $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_5\text{H}_5)_2$, the six sulfur and two nitrogen atoms attached to the plutonium center also described a distorted trigonal dodecahedron around the central Pu^{3+} ion. Within this polyhedron, the pyridine ligands occupied the “outer” sites of one of the two interpenetrating trapezoids.

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 ($68.7^\circ \pm 0.6$) for the larger Pu^{III} ion.

The distances and angles in the $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ complexes were very similar to those observed for the $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ complexes (Table 4). For example, the P–S and P–C distances were again ~ 2.01 and $\sim 1.80 \text{ \AA}$, and the S–P–S and S–M–S angles were $\sim 109^\circ$ and $\sim 70^\circ$. The average An–S distance of 2.85 ± 0.02 for U and $2.83 \pm 0.01 \text{ \AA}$ for Np were also essentially identical with those seen in their $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$ analogs. The major difference between the $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ and $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ structures was the C–P–C angle. For example, instead of the $\sim 105^\circ$ value seen for the $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$ complexes, this angle was reduced to $\sim 92^\circ$ in the $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ 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'-biphenylenedithiophosphinic acids, $\text{HS}_2\text{P}(\text{R}_2\text{C}_6\text{H}_4)$, where $\text{R} = \text{H}$ or tBu . These air and moisture stable salts are chemical relatives of the well-known class of diaryldithiophosphinates, some of

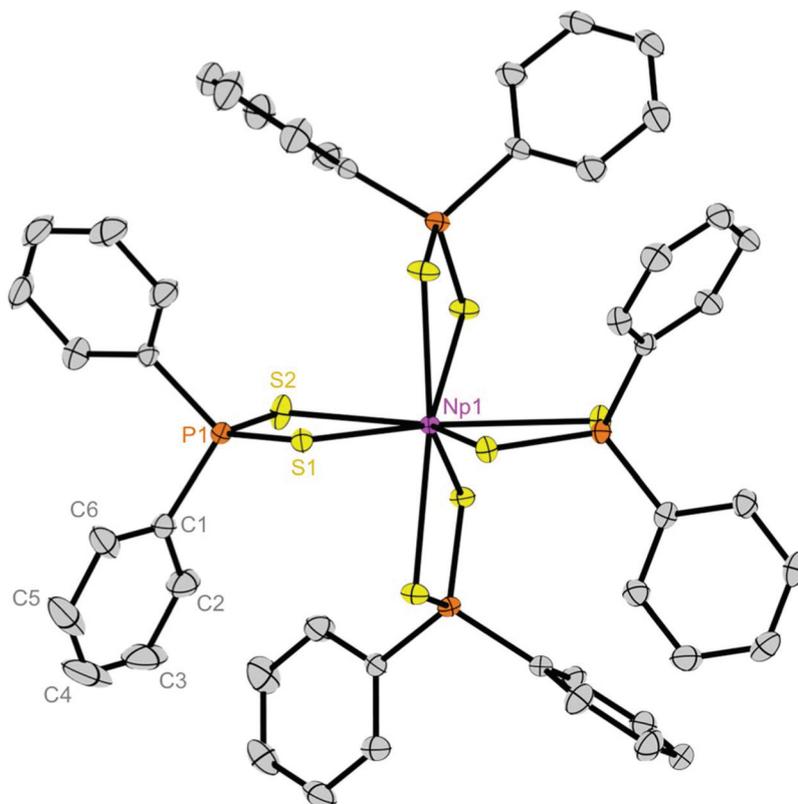


Fig. 4 Molecular structure of $\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$. Thermal ellipsoids show the 50% probability density surfaces. Hydrogen atoms and solvent molecules have been omitted.

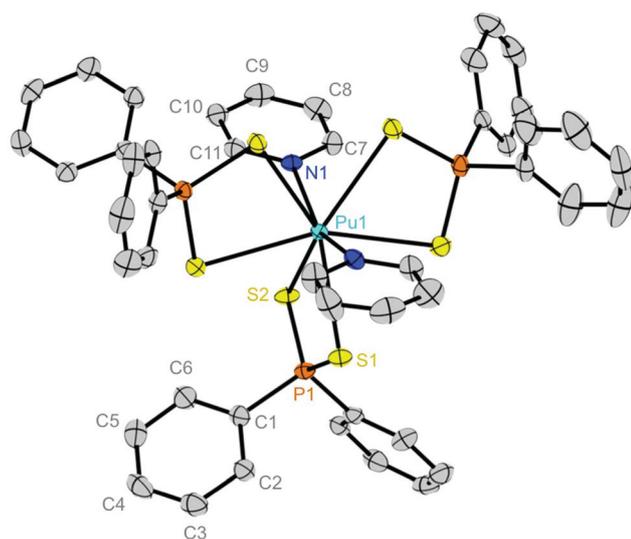


Fig. 5 Molecular structure of $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_5\text{H}_5)_2$. Thermal ellipsoids show the 50% probability density surfaces. Hydrogen atoms and solvent molecules have been omitted.

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 PC_4 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-5*H*-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 $\text{HS}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)$. These dithiophosphinic acids were readily deprotonated to the corresponding $\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)^{1-}$ anions, which were isolated as salts with tetraphenylpnictonium cations. The biphenylenedithiophosphinate salts represent interesting candidates for electronic structure studies (currently underway).

We also prepared five new actinide dithiophosphinate complexes, namely $\text{U}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]_4$, $\text{Np}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]_4$, $\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$, $\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$, and $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_5\text{H}_5)_2$. These new compounds were characterized and their structures determined by X-ray crystallography. Attempts to prepare the plutonium analogue using Pu^{IV} starting materials and $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$ produced a mixture of products from which we postulated a transient Pu^{III} species based on UV-vis spectroscopy. However, a stable trivalent plutonium compound, $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_5\text{H}_5)_2$, was isolated as single crystals from a

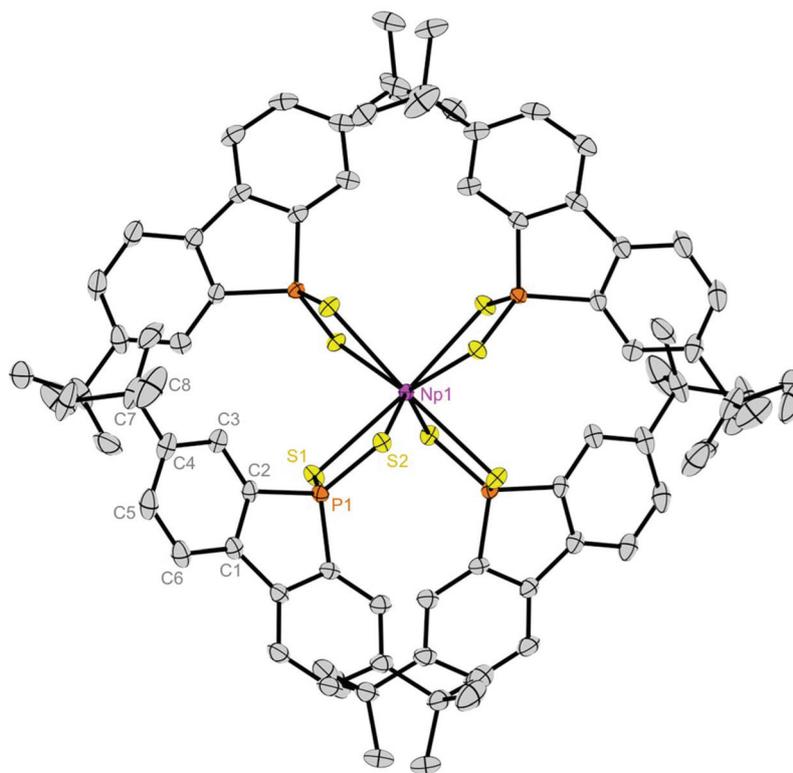


Fig. 6 Molecular structure of $\text{Np}[\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]_4$. Thermal ellipsoids show the 50% probability density surfaces. Hydrogen atoms and solvent molecules have been omitted.

Table 3 Crystallographic data for actinide dithiophosphate complexes

	$\text{U}[\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]_4 \cdot \text{toluene}$	$\text{Np}[\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]_4 \cdot 4\text{toluene}$	$\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot \text{THF}$	$\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot \text{THF}$	$\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_5\text{H}_5)_2 \cdot \text{toluene}$
Formula	$\text{C}_{87}\text{H}_{104}\text{P}_4\text{S}_8\text{U}$	$\text{C}_{108}\text{H}_{128}\text{NpP}_4\text{S}_8$	$\text{C}_{52}\text{H}_{48}\text{OP}_4\text{S}_8\text{U}$	$\text{C}_{52}\text{H}_{48}\text{NpOP}_4\text{S}_8$	$\text{C}_{53}\text{H}_{48}\text{N}_2\text{P}_3\text{PuS}_6$
Formula wt (g mol^{-1})	1768.09	2043.46	1307.29	1306.26	1237.29
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_12_12_1$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	17.760(3)	22.8029(17)	10.9621(7)	10.9835(9)	11.770(2)
b (Å)	19.279(4)	20.2642(15)	13.3551(9)	13.3013(10)	14.808(3)
c (Å)	25.446(5)	23.9268(17)	18.5207(12)	18.4912(14)	16.972(3)
α (°)	90	90	94.845(1)	94.945(1)	79.148(2)
β (°)	90	110.020(1)	95.092(1)	95.113(1)	70.433(2)
γ (°)	90	90	96.650(1)	96.364(1)	69.036(2)
V (Å ³)	8713(3)	10 388.1(13)	2670.2(3)	2661.5(4)	2594.8(8)
Z	4	4	2	2	2
ρ_{calcd} (g cm^{-3})	1.348	1.307	1.626	1.63	1.587
μ (mm^{-1})	2.17	1.268	3.51	2.424	1.642
Data/restraints/params	18 631/0/926	22 227/6/457	10 022/0/595	12 585/0/595	11 790/42/575
Goodness-of-fit on F^2	0.831	1.467	1.000	1.100	0.933
R_1 [$F^2 > 2\sigma(F^2)$]	0.0288	0.0500	0.0333	0.0223	0.0351
wR_2 (all data)	0.0482	0.1365	0.0913	0.048	0.0674
Largest $\Delta\rho$ (e Å^{-3})	0.595/−0.976	3.837/−3.013	3.587/−1.760	1.141/−0.613	1.154/−1.059

reaction between trivalent $\text{PuI}_3(\text{NC}_5\text{H}_5)_4$ and $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$. In contrast, in the presence of diphenyldithiophosphate, uranium and neptunium preferred the tetravalent oxidation state. These observations were consistent with reduction potentials reported for these elements (eqn (12)–(14)),^{40,42}

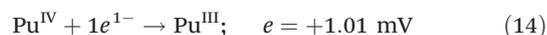
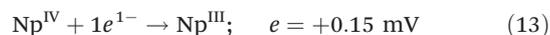
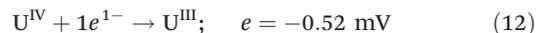
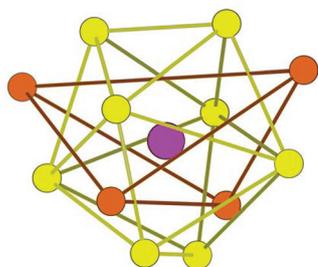


Table 4 Selected average bond distances and average angles for actinide dithiophosphate complexes. Error bars are given as standard deviations of the mean (at 1σ)

	U[S ₂ P(^t Bu ₂ C ₁₂ H ₆) ₄] ⁻ toluene	Np[S ₂ P(^t Bu ₂ C ₁₂ H ₆) ₄] ⁻ 4toluene	U[S ₂ P(C ₆ H ₅) ₂] ₄ ⁻ THF	Np[S ₂ P(C ₆ H ₅) ₂] ₄ ⁻ THF	Pu[S ₂ P(C ₆ H ₅) ₂] ₃ (NC ₅ H ₅) ₂ ⁻ toluene
M-S (Å)	2.85 ± 0.02	2.83 ± 0.01	2.85 ± 0.03	2.82 ± 0.03	2.93 ± 0.02
M-N (Å)	NA	NA	NA	NA	2.62 ± 0.01
P-S (Å)	2.001 ± 0.007	2.003 ± 0.006	2.014 ± 0.006	2.009 ± 0.003	1.997 ± 0.006
P-C (Å)	1.800 ± 0.007	1.794 ± 0.003	1.814 ± 0.005	1.809 ± 0.003	1.816 ± 0.006
C-C _{tether} (Å)	1.477 ± 0.005	1.477 ± 0.003	NA	NA	NA
C-C _{aryl} (Å)	1.39 ± 0.01	1.40 ± 0.01	1.39 ± 0.01	1.38 ± 0.01	1.38 ± 0.01
S-P-S (°)	109.4 ± 0.9	109.8 ± 0.1	109.4 ± 0.1	109.0 ± 0.1	111.8 ± 0.6
C-P-C (°)	92.4 ± 0.2	92.5 ± 0.3	105.2 ± 1.6	105.2 ± 1.3	104.1 ± 0.9
S-M-S (°)	70.0 ± 0.7	70.8 ± 0.1	70.6 ± 0.2	70.8 ± 0.1	68.7 ± 0.6

**Fig. 7** Ball and stick representation of Np[S₂P(^tBu₂C₁₂H₆)₄]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).

while the generality of these observations is yet to be established – especially in air and acidic media – the results provocatively suggest that the Pu^{III} oxidation state should be considered in other systems when in the presence of dithiophosphate extractants.

The structural metrics of the actinide dithiophosphate complexes suggested that the constraints imposed by the dibenzo[*b,d*]phosphole ring system in S₂P(^tBu₂C₁₂H₆)¹⁻ had few structural consequences, except the expected closing of the C–P–C angle in comparison to the untethered S₂P(C₆H₅)₂¹⁻ ligands. The electronic effects may be more significant, especially in view of our recent experimental and theoretical results, which indicated that the polarizability of diaryldithiophosphinates and their ability to discriminate between lanthanides and actinides is strongly influenced by subtle changes in the relative orientation of the aryl rings.^{43,44} 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.

Experimental section

General experimental considerations

Caution! The ²³⁸U isotope is a low specific-activity (primarily α -emitting radionuclide that decays to α -, β -, and γ -emitting isotopes. Its use presents hazards to human health. The ²³⁷Np and ²³⁹Pu 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 analyses of these hazards and implementation of controls for the safe handling and manipulation of these toxic and radioactive materials.

The starting materials UCl₄,⁴⁵ PuI₃(py)₄,⁴⁰ [PPh₄]₂[NpCl₆],⁴⁶ NpCl₄(DME)₂,⁴⁷ and U[N(SiMe₃)₂]₃⁴⁰ were prepared by means of literature-reported procedures. All reactions involving Pu and Np were performed inside an MBraun Labmaster 130 - glovebox filled with an 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 or 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.

Elemental analyses were carried out by the Micro-Mass facility at the University of California, Berkeley, and by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois, Urbana-Champaign. The infrared spectra were recorded on a Nicolet Magna-IR System 750 spectrometer or a Nicolet IR200 FTIR spectrometer as Nujol mulls between

KBr plates. The ^1H 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 (^1H) or H_3PO_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 6000i UV/vis/NIR spectrophotometer.

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

This procedure is a modification of a literature-reported recipe.²⁹ A solution of 2,2'-dibromobiphenyl (2.49 g, 7.98 mmol) in Et_2O (50 mL) was cooled to 0 °C and treated dropwise with $^n\text{BuLi}$ (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 $\text{BrP}(\text{C}_{12}\text{H}_8)$ and $\text{ClP}(\text{C}_{12}\text{H}_8)$ 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-5H-dibenzophospholes in toluene was used in subsequent reactions without further purification. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, toluene): δ 68.2 (s, ClPR_2), 49.3 (s, BrPR_2). Lit:²⁹ δ 69.0 (s, ClPR_2). The ratio of $\text{BrP}(\text{C}_{12}\text{H}_8)$ to $\text{ClP}(\text{C}_{12}\text{H}_8)$ was *ca.* 2:3 as judged from integration of the ^{31}P NMR spectrum.

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

To the above mixture of 5-chloro-5H-dibenzophosphole and 5-bromo-5H-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 aq. NaOH solution (to sequester evolved H_2S). 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_2Cl_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 $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$ in MeCN (75 mL) and allowing the solution to evaporate to approximately 20 mL. This procedure provided $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$ as pale yellow plates. Crystalline yield: 1.07 g (54% from 2,2'-dibromobiphenyl). ^1H NMR (400 MHz, CDCl_3): δ 7.98 (dddd, $J = 12.2, 7.5, 1.3, 0.7$ Hz, 2H, 3,3'-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). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 46.9 (s). HRMS m/z (EI^+). Calcd: 247.9883 [M^+]; found: 247.9883. IR (cm^{-1}): 3066 m, 2959 s, 2925 s, 2854 s, 2330 br m, 1592 w, 1470 m, 1439 s, 1377 w, 1269 w, 1157 w, 1128 m, 1066 m, 966 w, 841 w, 756 s, 722 s, 658 s, 617 w, 541 m, 520 w, 483 w, 449 m, 413 m.

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

A solution of $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$ (50.0 mg, 0.201 mmol) in aqueous NH_4OH (15 mL of a 3.6 M solution, 0.540 mmol) was treated dropwise in air with a solution of tetraphenylphosphonium 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_2O (3×5 mL). The solid was dissolved in a 1:1 mixture of acetone (5 mL) and H_2O (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 $\text{C}_{36}\text{H}_{28}\text{P}_2\text{S}_2$: C, 73.7; H, 4.81; P, 10.56; S, 10.93. Found: C, 73.5; H, 4.67; P, 10.46; S, 10.80%. ^1H NMR (500 MHz, $\text{d}_3\text{-MeCN}$): 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). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{d}_3\text{-MeCN}$): δ 61.1 (s, S_2PR_2^-), 24.4 (s, PPh_4^+). 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-5H-dibenzo[*b,d*]phosphole, $\text{ClP}(\text{Bu}_2\text{C}_6\text{H}_4)$

To 4,4'-di-*tert*-butylbiphenyl (10.65 g, 40.0 mmol) in hexane (75 mL) was added $^n\text{BuLi}$ (50 mL of a 1.6 M solution in hexanes, 80.0 mmol). To the mixture was added KO^tBu (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 at 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(^tBu₂C₁₂H₆)

To a solution of 3,7-di-*tert*-butyl-5-chloro-5*H*-dibenzophosphole (theoretical yield: 40 mmol) in toluene (50 mL) was added elemental sulfur (1.28 g, 5.0 mmol reckoned as S₈) against a counterflow of argon. The mixture was heated to reflux for 8 h. The resulting yellow solution was cooled to 25 °C and filtered to remove a small amount of yellow precipitate. The filtrate was 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 solid was treated with a solution of sodium hydrosulfide hydrate (7.47 g, *ca.* 80.0 mmol) 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 (ddd, *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). HRMS *m/z* (ESI⁺). Calcd: 361.1214 [M + H]⁺. Found: 361.1209. IR (cm⁻¹): 3047 w, 2924 s br, 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, 1300 w, 1272 w, 1255 m, 1156 m, 1110 m, 1084 w, 1061 m, 1084 w, 1061 m, 874 w, 829 s, 794 w, 733 s, 723 s, 671 s, 603 m, 535 s.

Tetraphenylarsonium 4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphinate, [AsPh₄][S₂P(^tBu₂C₁₂H₆)]

This compound was synthesized by treating a solution of HS₂P(^tBu₂C₁₂H₆) (100.0 mg, 0.277 mmol) in aqueous NH₄OH (20.0 mL, 3.6 M) with a solution of tetraphenylarsonium chloride hydrate (182 mg, 0.417 mmol) in H₂O (5.0 mL) as described above for [PPh₄][S₂P(C₁₂H₈)]. Purification was affected by slow evaporation of a 20 mL 1 : 1 acetone : H₂O solution to *ca.* 5 mL, which afforded large, pale yellow needles of [AsPh₄][S₂P(^tBu₂C₁₂H₆)]·0.5acetone that were suitable for X-ray diffraction. Yield: 95.2 mg (45%). Anal. Calcd for C_{45.5}H₄₇O_{0.5}AsPS₂: C, 70.8; H, 6.14; As, 9.71; P, 4.01; S, 8.31.

Found: C, 70.5; H, 6.03; As, 9.99; P, 4.12; S, 8.60%. ¹H NMR (500 MHz, d₃-MeCN): δ 7.89–7.84 (m, 4H, Ar-H), 7.77–7.66 (m, 18H, Ar-H), 7.63 (dd, *J* = 8.1, 3.2 Hz, 2H, 6,6'-CH), 7.42 (ddd, *J* = 8.1, 1.7, 1.7 Hz, 2H, 5,5'-CH), 1.35 (s, 18H, -C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, d₃-MeCN): δ 61.8 (s). IR (cm⁻¹): 3385 br, 3048 w, 2917 s, 2856 s, 1577 w. 1460 s, 1441 s, 1378 m, 1362 m, 1312 w, 1252 m, 1187 w, 1156 w, 1113 w, 1081 m, 1023 w, 997 m, 823 m, 749 s, 727 s, 789 m, 660 s, 584 m.

Potassium 4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphinate, K[S₂P(^tBu₂C₁₂H₆)]

To a cold (0 °C) solution of 4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphinic acid (2.15 g, 5.96 mmol) in toluene (20 mL) was added a solution of potassium hexamethyldisilazide (1.31 g, 6.57 mmol) in toluene (20 mL). The mixture, which became turbid, was stirred at 25 °C for 30 min. The white solid was collected by filtration, washed with cold (0 °C) toluene (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 7.77 (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 (ddd, *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. The microanalytical and IR data suggest the presence of the hydrate K[S₂P(^tBu₂C₁₂H₆)]·H₂O. Anal. Calcd for C₂₀H₂₆POS₂K: 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, 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.

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). The solid was dried under vacuum (10⁻³ Torr), collected as a white powder (460 mg; 82% yield), and used as K₂S₂P(C₆H₅)₂ for subsequent reactions.

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 (5 mL), and dried under vacuum to afford a green powder. Yield: 99.1 mg (64% based on the amount of U in the starting material). Anal. Calcd for C₄₈H₄₀P₄S₈U: C, 46.7; H, 3.24. Found: C, 46.7; H, 3.60. ¹H NMR (300 MHz, C₆D₆): δ 12.4 (s, 16H, 2,6-CH), 9.0 (t, *J* = 7.4 Hz, 16H, 3,5-CH), 8.7 (t, *J* = 7.5 Hz, 8H, 4-CH). ³¹P{¹H} NMR (121 MHz, C₆D₆): δ -581 (br s). UV/vis/NIR in THF solution (λ_{max}, nm): 336 sh, 353 sh,

395 sh, 423 sh, 471, 534 sh, 593, 630, 663 sh, 706 sh, 772, 875 sh, 919, 1020, 1081, 1112 sh, 1237, 1252 sh. IR (cm⁻¹): 481 sh, 486, 564, 612, 647, 687, 705, 743, 1099. Single-crystals of U[S₂P(C₆H₅)₂]₄·THF suitable for X-ray diffraction were obtained from a THF solution of U[S₂P(C₆H₅)₂]₄ into which 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 K₂S₂P(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(IV), Np[S₂P(C₆H₅)₂]₄

Method A. To [PPh₄]₂[NpCl₆] (6.6 mg, 0.006 mmol) was added a solution of K₂S₂P(C₆H₅)₂ (6.7 mg, 0.023 mmol) in THF (3 mL). The initially peach/salmon-pink mixture was stirred at ambient temperature for 2 h to give a deep red solution and a white precipitate (presumed to be KCl). The solution was filtered through a glass fiber filter circle. The deep red filtrate was concentrated under vacuum to 1.5 mL and Et₂O was vapor diffused into the solution at -35 °C. After 2 days, red block-shaped crystals of Np[S₂P(C₆H₅)₂]₄·THF had formed that were used for the X-ray diffraction study. ¹H NMR (300 MHz, CD₂Cl₂): δ 9.1 (s, 16H, 2,6-CH), 7.9 (s, 24H, 3,4,5-CH). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ -701 (br s). UV/vis/NIR (THF; λ_{max}, nm): 693, 744, 759, 780 sh, 789, 821, 856, 886, 922, 976, 1024. Solid-state diffuse reflectance UV/vis/NIR (λ_{max}, nm): 693, 746, 759, 790, 820, 856, 887, 920, 978, 1021.

Method B. To solid [PPh₄]₂[NpCl₆] (20.1 mg, 0.018 mmol) was added a solution of K₂S₂P(C₆H₅)₂ (20.5 mg, 0.071 mmol) in THF (3 mL). The mixture was heated at 50 °C for 30 min and then stirred at ambient temperature for 14 h. The resulting cloudy red solution was filtered through Celite on a glass fiber filter circle. The deep red filtrate was stored at -35 °C for 4 days to afford a red solid, which was collected, washed with hexanes (5 mL), and dried under vacuum. Yield: 7.1 mg (33%).

Method C. To a solid mixture of NpCl₄(DME)₂ (19.9 mg, 0.036 mmol) and K[S₂P(C₆H₅)₂] (41.1 mg, 0.143 mmol) was added THF (3 mL). The resulting deep red cloudy solution was stirred at ambient temperature for 2 days and then filtered through Celite supported on a glass fiber filter circle. The filtrate was taken to dryness under vacuum, and the resulting residue was dissolved in THF (1 mL) with heating at 50 °C for 5 min. The solution was filtered through a glass fiber filter circle, layered with Et₂O, and stored at -35 °C. After one day,

red crystals had deposited, which were collected and dried under vacuum. Yield: 12.6 mg (29%).

Tris(diphenyldithiophosphinato)bis(pyridine)plutonium(III), Pu[S₂P(C₆H₅)₂]₃(NC₅H₅)₂

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 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)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.

Tetrakis(4,4'-di-tert-butyl-2,2'-biphenylenedithiophosphinato)uranium(IV), U[S₂P(^tBu₂C₁₂H₆)]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'-dithiophosphinate (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. Calcd for C₈₀H₉₆P₄S₈U: C, 57.33; H, 5.77; P, 7.39; S, 15.30; U, 14.20. Found: C, 57.83; H, 5.92%. ¹H NMR (500 MHz, CDCl₃): δ 13.1 (s, 8H, 3,3'-CH), 8.49 (d, J = 7.6 Hz, 8H, 6,6'-CH), 8.26 (d, J = 7.6 Hz, 8H, 5,5'-CH), 2.55 (s, 72H, C(CH₃)₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ -603 (br s). IR (cm⁻¹): 2955 s, 2924 s br, 1462 m br, 1377 m, 1365 w, 1255 w, 1155 w, 1110 w, 1082 w, 1060 w, 1022 w, 826 w, 794 w, 724 m, 665 w, 654 w, 614 w, 587 m. Crystallization from a mixture of THF (1.5 mL), toluene (1.5 mL), and hexane (0.5 mL) afforded green prisms of U[S₂P(^tBu₂C₁₂H₆)]₄ that were suitable for X-ray diffraction.

Tetrakis(4,4'-di-tert-butyl-2,2'-biphenylenedithiophosphinato)neptunium(IV), Np[S₂P(^tBu₂C₁₂H₆)]₄

To solid NpCl₄(DME)₂ (22.6 mg, 0.040 mmol) was added a solution of potassium 4,4'-di-tert-butyl-2,2'-dithiophosphinate (64.8 mg, 0.162 mmol) in THF (3 mL). The deep red solution was stirred at ambient temperature for 16 h. Volatile materials were removed under vacuum, and the red residue was stirred with toluene (6 mL) at 40 °C for 10 min, causing some of the red product to dissolve although some of the red material remained undissolved. The red solution was filtered while warm through Celite supported on a glass fiber filter circle.

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%. ¹H 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{¹H} NMR (121 MHz, CD₂Cl₂): δ -715 (br s). UV/vis/NIR (THF; λ_{max}, nm): 480, 693, 714 sh, 745 sh, 773, 788, 814, 852, 893, 919, 971, 1025, 1284, 1322. Solid-state diffuse reflectance UV/vis/NIR (λ_{max}, nm): 482, 695, 714 sh, 747 sh, 772, 787, 815, 850, 891, 921, 971, 1016, 1024, 1283, 1323. 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(Bu₂C₁₂H₆)₄·4toluene 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 Cryoindustries low temperature device. Data for Np[S₂P(Bu₂C₁₂H₆)₄] 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 SHELXTL and Mercury.⁵⁰

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