Coordination chemistry of homoleptic actinide(IV) thiocyanate complexes

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Coordination chemistry of homoleptic actinide(IV) thiocyanate complexes

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Abstract: The synthesis, X-ray crystal structure, vibrational and optical spectroscopy for the eight-coordinate thiocyanate compounds, $[Et_4N]_4[Pu^{IV}(NCS)_8]$, $[Et_4N]_4[Th^{IV}(NCS)_8]$, and $[Et_4N]_4[Ce^{III}(NCS)_7(H_2O)]$ are reported. Thiocyanate was found to rapidly reduce plutonium to Pu^{III} in acidic solutions (pH < 1) in the presence of NCS^-. The optical spectrum of $[Et_4N][SCN]$ containing Pu^{III} solutions was indistinguishable from that of aquated Pu^{III} suggesting that inner sphere complexation with $[Et_4N][SCN]$ does not occur in water. However, upon concentration, the homoleptic thiocyanate complex $[Et_4N]_4[Pu^{IV}(NCS)_8]$ is crystallized when a large excess of $[Et_4N][NCS]$ is present. This compound, along with its U^{IV} analogue, maintains inner-sphere thiocyanate coordination in acetonitrile based on the observation of intense ligand to metal charge transfer bands. Spectroscopic and crystallographic data do not support the interaction of the metal orbitals with the ligand pi-system, but support an enhanced An^{IV}-NCS interaction as the Lewis acidity of the metal ion is changed from Th to Pu.

Introduction

Despite their periodic classification as f-elements, there are considerable differences in the chemical behavior of the lanthanide and actinide elements. Increases in the covalent character of the actinide ligand bond have been cited as a potential explanation for these phenomenon since Diamond, Street, and Seaborg first proposed, in 1953, 5f orbital hybridization to explain the unusual elution pattern of actinide chlorides from an ion-exchange column.[1] However, numerous studies conducted in the intervening decades suggest that covalent bonding in actinides is often subtle, not necessarily correlated with thermodynamically strong bonds, and difficult to disentangle from the electrostatic interactions which dominate bonding in both lanthanide and actinide complexes.[2] Therefore, detailed studies of simple actinide coordination compounds remain a topic of great interest.[3]

Actinide complexes of soft-donor ligands (based on N, S, P, etc.) are one area where careful structural and spectroscopic studies have much to contribute to understanding the coordination chemistry of the actinide elements. Complexes containing soft-donors, including thiocyanate,[4] have been widely demonstrated to promote separation of trivalent actinides from lanthanides.[5] However, there is still much to be learned about the chemical origins of this enhanced separation in both the metal-ligand interactions, and the formation of supramolecular assemblies in such complex systems.[6]

From the point of view of the metal-ligand interaction, several studies have suggested that the origin of this selectivity is related to fundamental differences between lanthanide and actinide thiocyanate coordination because selective separation is observed across a wide variety of aqueous/organic phase compositions and extractant molecules.[7] In addition to the hypothesis promoting increased covalent character in the actinides, a greater tendency towards inner sphere coordination for actinides versus lanthanides has also been proposed.[7c, 8]

Evidence presented to support enhanced inner sphere coordination of actinides was based on complexation free energies[7e, 9] and stability constant data[7a, 7b, 7d, 8a, 10] determined from solvent extraction experiments. However, K_d and β values contain no structural information and cannot be reliably used as the sole source of data to explain the preferential binding of thiocyanate to actinides. For example, high energy X-ray scattering studies on chloride solutions demonstrate that while the metal ions do coordinate chlorine atoms in the first coordination sphere,[11] the measured stability constants are relatively unaffected by, and do not indicate the location (1st or 2nd coordination sphere) of the chlorine atoms associated with the metal center.[12] These are findings which cast doubt on the validity of simplifications used to infer structural information from solvent extraction data and bulk thermodynamic quantities. For this reason, the isolation and characterization of lanthanide and actinide thiocyanate compounds have much to contribute towards understanding the chemical differences between the actinide- and lanthanide-ligand interaction.

A variety of lanthanide thiocyanates have been previously reported.[13] In each case, the thiocyanate is N-bound, displaying the same coordination mode as other “hard” metals.[10a, 14] To date, few examples of isolable actinide thiocyanate complexes have been reported, with the majority of work conducted on thorium and uranium compounds.[15] These compounds are also N-bound and display many structural similarities to their lanthanide analogues. The uranyl thiocyanates $[R_4N]_3[UO_2(NCS)_5]$ (R = Me–Pr) have been studied, and Raman spectroscopy data suggest weak thiocyanate complexation as an equilibrium between free and bound thiocyanate is established in aqueous solution.[15e] Additionally, the homoleptic compounds $[Et_4N]_4[Th(NCS)_8]$ (**Th-NCS**) and $[Et_4N]_4[U(NCS)_8]$ (**U-NCS**), are of particular interest as complicating variables introduced by a heteroleptic coordination environment are eliminated, allowing a direct examination of the actinide-thiocyanate interaction.[15a, 15d-f]

There have only been a handful of studies detailing the synthesis and properties of transuranic thiocyanate compounds.[15f, 16] One notable report describes a series of

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complexes which share the formula $[Et_4N]_4[An(NCS)_8]$ (An = Pa–Pu).[15f] All four compounds crystallized in a body-centered tetragonal cell and were presumed to possess the same cubic coordination about the actinide as **U-NCS**.[15b] However, analysis was limited to an examination of diffraction photographs[15f] which precludes a detailed comparison of structural metrics. Rao and coworkers later suggested that Pu^{III} is the only oxidation state of Pu to be expected in the presence of thiocyanate due to the ligand's redox activity.[16b] Obviously, this claim conflicts with the structure of $[Et_4N]_4[Pu^{IV}(NCS)_8]$ (**Pu-NCS**) originally assigned.[15f] Additional confusion arises from a report describing trivalent lanthanide compounds with the formula $[Et_4N]_4[Ln^{III}(NCS)_7(H_2O)]$ which crystallize in a tetragonal lattice[13b] that would be indistinguishable from those observed for the $[Et_4N]_4[An(NCS)_8]$ complexes using the characterization methods employed by Bagnall and Brown.[15f]

The confusion surrounding the redox behavior of plutonium with NCS^- is of particular interest considering the application of this chemistry for the separation of trivalent lanthanides and actinides.[4] Despite this fact, all of the detailed structural studies done to date have examined complexes in higher oxidation states. This makes plutonium an interesting candidate for further study as both Pu^{IV} and Pu^{III} are stable if appropriate conditions are selected. Considering the redox properties of thiocyanate, we saw isolation of Pu^{III} and Pu^{IV}-NCS complexes as a promising opportunity to study how the behavior of actinide thiocyanates differs among the early actinide elements.

Results and Discussion

In an effort to further explore Pu/NCS^- redox chemistry in aqueous solutions, we elected to study the absorption spectrum of Pu thiocyanate solutions. As reported by Rao,[16b] when a Pu^{IV} solution in 1 M HCl was combined with 11.6 equivalents of $[Et_4N][SCN]$ the solution turns from orange to the characteristic blue color of Pu^{III} within 10 minutes. This observation is also in agreement with the reported +780 mV (vs. Ag/AgCl) cathodic potential for $[Et_4N][NCS]$ oxidation versus the +980 mV $Pu^{IV/III}$ couple in $HClO_4$.[10b, 16b, 17] The observed UV-Vis spectrum was indistinguishable from that of independently prepared aquated Pu^{III} (Figure 1) obtained by treating Pu^{IV} with $NH_2OH{\cdot}HCl$.[17a, 17b].

Before abandoning our attempts to isolate a Pu^{III}-NCS complex, we wanted to assess whether redox induced decomposition of the thiocyanate could be inhibiting coordination. This was accomplished by reacting solutions of valence pure Pu^{III} (prepared by addition of $NH_2OH{\cdot}HCl$ to a $^{242}Pu^{IV}$ stock solution) with $[Et_4N][SCN]$ (11 equivalents). When this reaction was attempted in 1 M HCl, crystals of $[Et_4N][Pu(H_2O)_6Cl_2]Cl_2{\cdot}2H_2O$ were isolated in lieu of the desired NCS^- compound.[18] This is likely due to significant competitive ligation of Cl^- as the free energy of thiocyanate complexation with actinides is very small (e.g. -0.813 kcal mol^{-1} for Am^{III}).[7e] In an effort to circumvent this, we repeated the reaction in 3.3 M trifluoromethanesulfonic acid, as the $CF_3SO_3^-$ anion is not expected to be a competitive inner-sphere ligand in aqueous

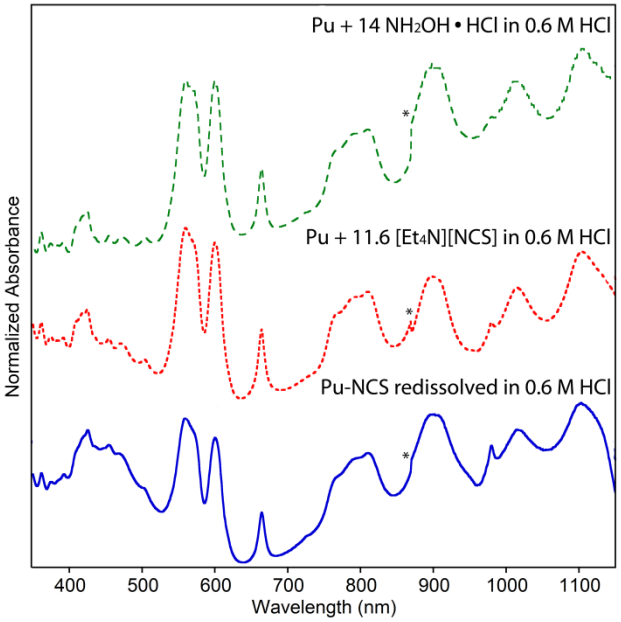


Figure 1. UV-Vis spectrum from 350-1150 nm of Pu^{III} solutions prepared by independent synthesis (top), addition of $[Et_4N][NCS]$ (middle), and dissolution of **Pu-NCS** in 0.6 M HCl (bottom).

solution.[19] However, studies have shown that triflate and other ions typically considered "non-coordinating" can bind lanthanides in non-aqueous solutions and ionic liquids.[20] In our study, despite the presence of a large excess of thiocyanate, crystals of a sulfonate bridged 1-D oligomer $[Pu((CF_3)SO_3)_3(H_2O)_3]$ (**Pu-OTf**, Figure S-10) were obtained when the solution was allowed to concentrate by evaporation. These results, when considered together with the optical spectra in Figure 1, indicate that significant inner-sphere thiocyanate coordination to Pu^{III} does not occur in acidic aqueous environments.[21]

In the context of these data, we were intrigued to observe the deposition of a red crystalline compound from solutions of Pu^{III} and NCS^- to which no exogenous reductant had been added. X-ray diffraction studies revealed that this red compound matched the reported tetragonal until cell of **Pu-NCS**. The identity of the bulk material was confirmed by matching the powder X-ray diffraction pattern, Figure S-1, with the simulated pattern from single crystal diffraction data, Table 1, Figure 2. Crystals of **Pu-NCS** were studied using single crystal X-ray diffraction and the refinement confirmed a cubic environment around Pu(1) with eight coordinated thiocyanates. With these data, the oxidation state of the Pu center could be unambiguously assigned as Pu^{IV}, based on the presence of four Et_4N^+ cations in the unit cell. Additional confirmation was obtained from the Raman spectrum where only two C-N stretches were observed (see below for details). Convinced that **Pu-NCS** is indeed a Pu^{IV} compound, we next sought an explanation as to how a Pu^{III} thiocyanate solution, in which inner sphere complexes are not observed, could produce crystals of a homoleptic, coordinatively saturated, Pu^{IV} complex.

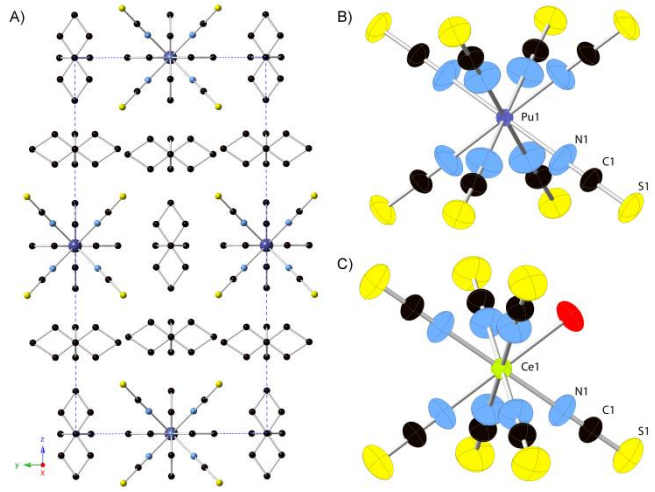
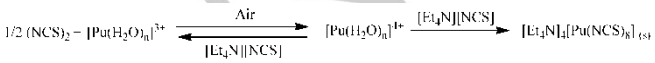


Figure 2. A) Tetragonal packing of **Pu-NCS**, **B)** Coordination environment of **Pu-NCS**. **C)** Coordination environment of **Ce-NCS**. All thermal ellipsoids shown at 50% probability.

To rationalize this, we propose a hypothesis based on consideration of the aqueous redox chemistry of plutonium[17c, 22] and Le Chatelier's principle, Scheme 1. From the previous isolation of **U-NCS**[15b] and **Th-NCS**,[15a, 15f] it stands to reason that complexation of NCS^- to Pu^{IV} would be more favorable than for Pu^{III}. We also suggest that, even in the presence of thiocyanate, Pu^{III} is partially re-oxidized in air in the same manner as simpler aqueous solutions of plutonium.[22] Any Pu^{IV} that is formed is presumably re-reduced by thiocyanate. However, this type of redox cycle likely leads to a small equilibrium population of Pu^{IV} in solution. Since NCS^- ligation is favored for Pu^{IV}, this creates a situation wherein **Pu-NCS**, which is sparingly soluble in aqueous solutions, is continuously removed by crystallization. This has the effect of producing additional Pu^{IV} in the solution and driving the desired reaction. Further evidence to support complexation and crystallization shifting the $Pu^{III/IV}$ equilibrium was obtained when the supernatant, from which the **Pu-NCS** crystals were obtained, was diluted in $HClO_4$. A ligand-to-metal charge transfer band at 360 nm was observable (see below, Figure 4, Figure S-11). Scintillation counting, and the previously reported molar absorptivities of Pu(III), were used to estimate that approximately 6% of the Pu remaining in solution was present as NCS^- ligated Pu^{IV}. Additionally, when **Pu-NCS** was re-dissolved in 0.6 M HCl, the optical spectrum of this solution was identical to those obtained in our previous experiments, Figure 1, indicating that the plutonium is rapidly reduced upon dissolution.

To obtain a better understanding of how the Pu-NCS interaction compares to that in other actinide and lanthanide



Scheme 1. Proposed speciation of **Pu-NCS** in aqueous solution and in the solid state.

Table 1. Crystallographic properties of homoleptic actinide thiocyanates.

Compound	**Th-NCS**	**Pu-NCS**	**Ce-NCS**
Formula	$C_{40}H_{80}N_{12}S_8Th$	$C_{40}H_{80}N_{12}S_8Pu$	$C_{39}H_{82}N_{11}OS_7Ce$
Mw (g mol^{-1})	1217.7	1227.6	1085.7
Lattice Type	Tetragonal	Tetragonal	Cubic
Space Group	I4/mmm	I4/mmm	Pm-3m
a/b (Å)	11.639(1)	11.620(1)	11.532(1)
c(Å)	23.164(1)	22.921(1)	11.532(1)
α/β/γ (°)	90.00	90.00	90.00
V ($Å^3$)	3138.0(3)	3095.1(4)	1533.6(2)
Z	2	2	1
ρ_{calc} (g cm^{-1})	1.289	1.317	1.176
T (K)[a]	300	300	300
λ (Å) [Mo kα]	0.71073	0.71073	0.71073
μ (mm^{-1})	2.677	1.370	1.015
S (GOF)	1.263	1.179	1.192
$R(F_o)$, $wR(F_o^2)$	0.03, 0.08	0.02, 0.07	0.05, 0.18
An-N (Å)	2.455(4)	2.364(4)	2.506(10)
$N\text{-}C_{NCS}$ (Å)	1.152(5)	1.152(4)	1.165(12)

[a] Data were collected at both 100 and 300 K. The 300 K data are listed here to allow comparison with data for **U-NCS** which were collected at room temperature.[15b] The data collected at 100 K are available in the supporting information.

complexes, the analogous Th compound (**Th-NCS**),[15a, 15f],[23] was also prepared, and the crystal structure of the tetragonal phase solved and refined. The structurally similar cerium complex $[Et_4N]_4[Ce^{III}(NCS)_7(H_2O)]$ (**Ce-NCS**),[13b] was also studied as an example of a redox-active metal which is expected to be exclusively trivalent in the presence of thiocyanate due to the highly oxidizing potential (1.4 V vs. NHE) of the $Ce^{IV/III}$ couple.[17a, 17b] As in the original report,[13b] water was assigned to a single coordination site (see experimental details). Despite the heteroleptic nature of the metal coordination environment, the X-ray data were best indexed to a primitive cubic lattice with a = 11.532(1) Å. The $Ln(SCN)_7(H_2O)^{4+}$ fragment does not have a preferred packing orientation causing the water to be disordered over all eight ligand sites giving rise to effective cubic symmetry at the metal center.

For all of the reported compounds, the N-C (1.15-1.16 Å) and C-S (1.55-1.59 Å) distances are the same within the error, Table 1. This observation can be rationalized by the central position of N-bound thiocyanate within in the spectrochemical series. A metal ligand bond wherein N-σ donation is the primary interaction is expected. By extension, little or no covalent orbital

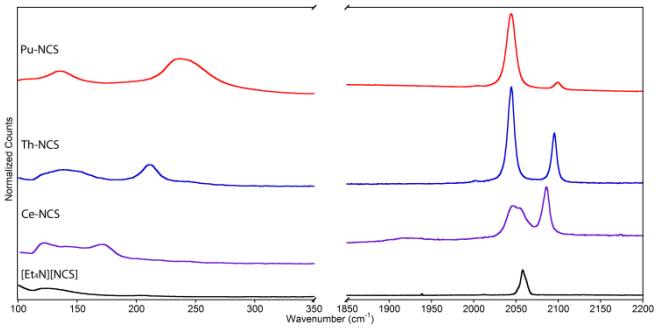


Figure 3. Raman spectra in the M-N and N=C stretching region collected on single crystals of **Th-NCS**, **Pu-NCS**, **Ce-NCS**, and $[Et_4N][NCS]$.

overlap of the metal orbitals with the NCS^- π-system is expected, or manifested in the crystallography. This is supported by the invariant N-C and C-S distances, as significant changes in interatomic distances are only expected when significant π-overlap is observed.[24]

In contrast to the N-C and C-S distances, a progressive decrease in the An-N bond distance for **Th-NCS**, **U-NCS**,[15c] and **Pu-NCS** (2.445(4), 2.38(1), 2.364(4) Å) is observed as the An^{IV} metals decrease in ionic radius,[25] and increase in relative Lewis acidity.[26] Additionally, the Ce-N bond distance (2.506(10) Å) in **Ce-NCS** is longer than for any of the actinides; as expected for a less Lewis-acidic trivalent ion with a larger ionic radius. While these changes in the M-N bond distances are significant, the crystallographic data alone cannot unambiguously decouple the combined effect of changing metal ligand interactions and bond distance effects which are solely a function of changing ionic radii. In fact, the difference between the sum of the Shannon radii[25] and the experimental data reveal a shortening of only 0.06-0.08 Å from the bond lengths expected for a purely ionic interaction for all three complexes. This indicates that a more sensitive probe into the dynamics of the M-N bond is necessary to gauge the effect of the identity and electron configuration of the metal ion.

To obtain an additional measure of the strength of the An^{IV}-NCS interaction, the Raman spectra of **Th-NCS**, **Pu-NCS**, and **Ce-NCS** were collected (Table 2). The Raman spectrum also allows for unambiguous differentiation of trivalent and tetravalent oxidation states for the metal ions based on the symmetry about the metal. For instance, **Th-NCS**, which is unquestionably Th^{IV}, possesses D_{4h} symmetry wherein all eight thiocyanate ligands experience a nearly identical coordination environment. Accordingly, only two C–N stretching modes (2044 and 2095 cm^{-1}) are observed. In contrast, **Ce-NCS** possesses C_{3v} site symmetry as each molecule within the crystal has seven thiocyanate ligands and a single coordinated water in fixed positions. This gives rise to three chemically distinct thiocyanate environments. Not surprisingly, a third Raman active mode is observed (2046, 2056, 2086 cm^{-1}) for this lower symmetry species. As previously discussed, **Pu-NCS** shows only two C=N stretching modes (2044 and 2099 cm^{-1}) providing further confirmation that the Pu center is in a 4^+ oxidation state

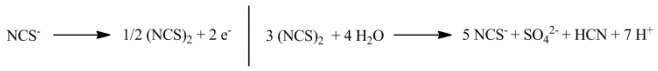
The C-N stretching frequencies for **Th-NCS**, **U-NCS**, and **Pu-NCS** differ by only 3-4 cm^{-1} across the early actinide series (Table 2, Figure 3), indicating that the changing identity of the metal ion has little effect on the thiocyanate π-bonds. This is consistent with the crystallographically determined C=N and C=S bond distances, and serves as further indication that covalent overlap and interaction with the ligand π-system is not a significant contributor to the An^{IV}-NCS interaction.

Table 2. Raman spectroscopy data for An^{IV} thiocyanate complexes.

Compound	C=N Stretch (cm^{-1})	C=S Stretch (cm^{-1})	M-N Stretch
Th-NCS	2044, 2095	888, 903	214
U-NCS[15c]	2047, 2099	Not Reported	Not Reported
Pu-NCS	2044, 2099	892, 903	246
Ce-NCS	2046, 2056, 2086	891, 904	176
$[Et_4N][NCS]$	2058	892, 906	N/A

An additional benefit of Raman spectroscopy is the ability to resolve lower frequency bands including M-N stretching frequencies.[27] Examining these bands allows a more direct probe into the strength of the An-NCS interaction, as any observed change in the frequency of the M-N bond will be indicative of a change in force constant.[28] When the An^{IV}-N stretching frequencies for **Th-NCS** (214 cm^{-1}) and **Pu-NCS** (246 cm^{-1}) are compared, the relative energy of the band and acidity of the metal ion appear to be correlated. The trend is also observed for **Ce-NCS**[29] which has a much lower M-N frequency (176 cm^{-1}); as expected from the reduction in oxidation state and corresponding decrease in acidity. Based on the primarily σ-donor character of the NCS^- ligand, this trend is also an indication that the strength of the M-NCS interaction is increasing across the actinide series from Th-Pu. However, the results obtained for **Ce-NCS** indicate that a significant decrease in the strength of the An-N interaction occurs for trivalent ions which is consistent with the apparent lack of NCS^- coordination to Pu^{III} in acidic solutions.

In order to examine the effect of thiocyanate coordination on the electronic structure of plutonium, we collected the solid state optical spectrum of **Pu-NCS**. When powdered **Pu-NCS** was affixed to a glass slide and the spectrum measured, no discrete bands were resolved in the 400-1,200 nm range. This result is rationalized by considering that the Pu center has a cubic coordination environment in which the f-f transitions, typically observed in actinide ions,[26a] are LaPorte forbidden due to the presence of inversion symmetry.[30] As these bands are often weak, (ε < 200 L mol^{-1} cm^{-1}) even in complexes without an inversion center, it is not surprising that they were not detected in the solid state spectrum, particularly in the presence of an intense and broad band observed in the UV. The absence of detectable f-f transitions in the solid state suggests that the deep red color of **Pu-NCS** is attributable to the charge transfer bands (see below) whose broad shoulder



Scheme 2. Summary of thiocyanate oxidation (left) and thiocyanogen disproportionation (right) processes.

extends well into the visible, absorbing in the blue/green region and giving rise to the reflected red color .

In order to better resolve the features of the absorption spectrum, we elected to obtain the solution spectrum of **Pu-NCS** in acetonitrile. Acetonitrile was selected due to the documented distortion of **U-NCS** to square antiprismatic upon dissolution in organic solutions.[15c, 15f] This has the effect of removing the inversion symmetry making the f-f transitions allowed. We anticipated that **Pu-NCS** would exhibit similar behavior and that the extended optical window of acetonitrile would allow for collection deeper into the near-UV region where absorption is expected give rise to the red color.

Additionally, we hypothesized that **Pu-NCS** would be significantly more stable as Pu^{IV} in organic solutions as the commonly accepted mechanism for thiocyanate oxidation is a binuclear process that yields two reducing equivalents and thiocyanogen, $(NCS)_2$, which is rapidly consumed via disproportionation in aqueous solution (Scheme 2).[31] Since competitive ligation by water will not occur in acetonitrile, the thiocyanate is more likely to remain bound in solution, preventing dimerization to thiocyanogen which should significantly increase the kinetic barrier for thiocyanate reduction of Pu^{IV}.

The UV-vis spectrum of **Pu-NCS** collected in acetonitrile (Figure 4A-B), contains features similar to that of Pu^{IV} in 1 M $HClO_4$.[17c] The spectrum also prominently features intense charge transfer (CT) bands at 266 nm, 357 nm (ε = 2130 L mol^{-1} cm^{-1}) and, 422 nm (1670 L mol^{-1} cm^{-1}). These features are not observed in the absence of SCN^- and are a strong indication that inner sphere coordination is maintained on dissolution in acetonitrile. The first of these bands can be attributed to a NCS^- n → π* band which is slightly shifted from the ~250 nm onset observed for the free ion. This band is also present in **Th-NCS** (Figure 4B) and **U-NCS**[15d] at similar energy, consistent with a primarily ligand based transition.

The latter two bands are assigned as NCS^- → $Pu_{(f)}$ based on the bathochromic shift compared to those observed for **U-NCS** at 276 (ε = 7600 L mol^{-1} cm^{-1}) and 340 nm (ε = 1800 L mol^{-1} cm^{-1}).[15d] These excitations are not observed in the absorption spectrum of **Th-NCS** (Figure 4A) which displays only the NCS^- n → π* CT band at 256 nm. The lack of a second NCS^- → $Th_{(f)}$ band is likely due to the higher energy of the f-orbitals at Th, which would push the band deep into the UV region. Conversely, a hypsochromic shift would be expected if these transitions were NCS^- → $An^{IV}_{(d)}$ or An^{IV} → NCS_{π^*}. This evidence is also in agreement with electrochemical and computational studies conducted on **U-NCS** demonstrating a SCN^- based HOMO and a uranium 5f based LUMO.[15d] The spectrum of **Ce-NCS** shows a single band at 314 nm, which is assigned as an f-f transition due to the similar wavelength and molar absorptivity as

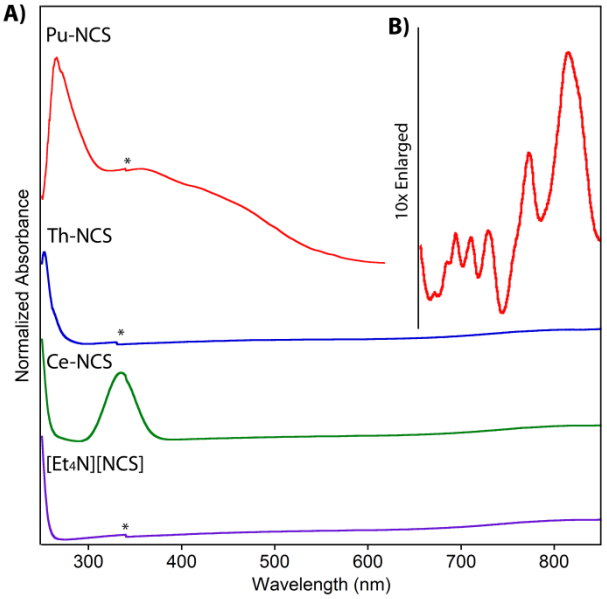


Figure 4. A) UV-Vis spectrum from 250-800 nm of (top to bottom) **Pu-NCS**, **Th-NCS**, **Ce-NCS**, and $[Et_4N][NCS]$ dissolved in acetonitrile (all solutions 2-5 mM). **B)** UV-Vis spectrum from 850-600 nm of 11.3 mM solution of **Pu-NCS** in acetonitrile. *Spectrophotometer grating change.

compared to previously reported data on cerium bromide complexes.[32] We are currently investigating whether this is a result of the CT band being shifted out of the accessible spectral window, or, if the band has disappeared due to displacement of the thiocyanate from the trivalent lanthanide center.

The progressive shift to lower energy of the charge transfer band in these compounds is consistent with the decrease in f-orbital energy from the early to the late actinides and demonstrates that the observed bands are ligand to metal charge transfer events. The observation of these CT bands in **U-NCS** and **Pu-NCS** is a strong indication of inner-sphere complexation, and illustrates that inner sphere thiocyanate coordination is persistent in non-aqueous solutions for tetravalent actinide ions. Additionally, the lack of competitive ligation by water has effectively disrupted the thiocyanate mediated redox reaction with plutonium.

Conclusions

The homoleptic thiocyanate complex **Pu-NCS** was prepared, and its complete X-ray crystal structure and Raman spectrum were reported for the first time. These studies, in concert with solution UV-vis data, were used to gain new insight into the coordination chemistry of plutonium in systems relevant to soft donor solvent extraction systems. It was determined that the predominant oxidation state of plutonium with NCS^- (in acidic media) is Pu^{III}. Furthermore, the electronic spectra suggest that inner sphere coordination of thiocyanate to Pu^{III} does not occur in aqueous systems to an appreciable extent. Our findings

suggest however, that a small equilibrium population of Pu^{IV} exists in solution causing crystallization of **Pu-NCS** which is stable and persistent as Pu^{IV}. Furthermore, **Pu-NCS** maintains inner sphere coordination in acetonitrile solution, based on the observation of intense charge transfer bands in the absorption spectrum, indicating that inner sphere thiocyanate coordination to An^{IV} ions is persistent in organic phases. Data from the vibrational spectra and X-ray crystallographic studies do not support the interaction of the metal orbitals with the ligand π-system as evidenced by the invariant C-N and C-S vibrational frequencies and bond distances. However, the same data support an enhanced An^{IV}-NCS interaction as the Lewis acidity of the metal ion is changed from Th to Pu.

Though we were unsuccessful in isolating a Pu^{III} thiocyanate complex, the observation that weak complexants (Cl^-, and OTf^-) bind preferentially to trivalent Pu in the presence of large excesses of SCN^- is an interesting result in its own right. In light of these results, the persistence of inner sphere coordination in aqueous and organic phases for trivalent f-elements remains an important question. As such, future work in our laboratory will seek to study thiocyanate complexes of actinides with more stable trivalent oxidation states, and to compare that data with analogous lanthanide complexes in a continued effort to understand the underlying chemical causes of soft donor enhanced selectivity in lanthanide/actinide separations.

Experimental Section

Caution! The reported compounds contain α-emitting radionuclides. All experiments described here were performed in a laboratory specially designed for the handling of α-emitting radionuclides including radiological fume hoods and gloveboxes under the supervision of health physics personnel.

General Methods. All chemicals and solvents, unless otherwise noted, were obtained from commercial sources and used as received. $[Et_4N][NCS]$ was prepared by combining ethanolic solutions of commercially available KNCS and $[Et_4N]Cl$ (in a 1:1 ratio) and removing the resulting KCl precipitate by filtration. The solution was then evaporated to dryness to give $[Et_4N][NCS]$ as a white powder which was used for use in synthesis and spectroscopic studies.

^{242}Pu Stock Solution. A ^{242}Pu stock solution was prepared using standard ion exchange methods.[22a] A solution of 120 mg ^{242}Pu in 7.5 M HNO_3 was loaded onto a Dowex anion exchange column which had been conditioned with 1 M HNO_3. Then, 60 ml of 1 M HNO_3 was run through the column to remove any other trace metals and ensure complete anion exchange. After washing the colum with HNO_3, 60 ml of 1 M HCl was used to elute the plutonium. This solution was boiled, and ~10 ml 35% HCl was periodically added to remove any residual nitrate as NO_2. When the evolution of NO_2 stopped, the solution volume was reduced to 5 ml. Heating was stopped, and the resulting 110 mM (determined by scintillation counting) solution of Pu^{IV} in HCl was used without further purification.

Synthesis of $[Et_4N]_4[Pu(NCS)_8]$ (Pu-NCS):

Route A: 188 μL (0.021 mmol) of a 110 mM $^{242}Pu^{IV}$ stock solution in 6 M HCl was diluted with 940 μL of deionized water. To this was added 233 mg (1.23 mmol, 60 equivalents) of $[Et_4N][NCS]$ dissolved in 1 mL of methanol. The mixture was allowed to stand open for 48 h leading to the formation of rectangular red crystals of **1**. The supernatant was removed, and the solid was allowed to dry in the dessicator for 24 h. The solids were then dissolved in acetone and allowed to recrystallize by slow evaporation over a ~12 h period. The yield was 13.2 mg (0.011 mmol, 52%) as determined by scintillation counting of the supernatant and the re-dissolved crystals.

Route B: 300 μL (0.021 mmol) of a 69 mM $^{242}Pu^{IV}$ stock solution in 6 M HCl was mixed with 117 mg (0.62 mmol, 30 equivalents) of $[Et_4N][NCS]$ dissolved in 3 mL of methanol. The mixture was allowed to stand open for 48 h leading to the formation of rectangular red crystals of **1**. The nearly colorless supernatant was removed, and the solid was suspended in dichloromethane and transferred to a filter paper to dry.

Note that solutions of **Pu-NCS** and **Th-NCS** in organic solvents will precipitate polythiocyanogen (SCN_n) if allowed to stand for extended periods of time. This material is highly insoluble, however, and readily removed from the mixture by decanting and recrystallizing the thiocyanate complex.

Synthesis of $[Pu(CF_3SO_3)_3(H_2O)_3]$ Oligomer (Pu-OTf): 200 μl (22 mmol) of an 110 mM $^{242}Pu^{IV}$ stock solution was treated with dropwise with a 2 M NH_2OH•HCl solution until the solution was visibly blue. Concentrated NH_4OH was then added drop-wise until precipitation of plutonium(III) hydroxide was observed. The solid was isolated by centrifuging the mixture and removing the supernatant with a pipet. The solid was then washed 3 times with 5 ml of water. After the final wash, the solid was dissolved in 0.55 ml of 3.33 M triflic acid and 5 drops of 2 M NH_2OH•HCl solution was added to maintain oxidation state purity. Long, deep-blue, needles of **Pu-OTf** were obtained by allowing this solution to concentrate for 48 h by evaporation. Note that the reaction produced **Pu-OTf** with or without added $[Et_4N][NCS]$.

Synthesis of $[Et_4N]_4[Th(NCS)_8]$ (Th-NCS): Compound **Th-NCS** was prepared by an alternative method to that reported by Bagnall, Brown, and coworkers.[15f] $Th(NO_3)_4$ was combined with an excess (10 equivalents) of $[Et_4N][NCS]$ in methanol and allowed to evaporate to dryness. The excess NCS^- salt was removed by washing with CH_2Cl_2 and pure **Th-NCS** was obtained by recrystallization from methanol following washing. The isolated compound matched previously reported characterization data.

Synthesis of $[Et_4N]_4[Ce(NCS)_7(H_2O)]$ (Ce-NCS): Compound **Ce-NCS** was prepared by the method of Ouchi and coworkers[13b] with the exception that $[Ce(H_2O)_7]Cl_3$ was substituted as the starting material and 10 equivalents of $[Et_4N][NCS]$ were utilized. The excess NCS^- salt was removed by washing with CH_2Cl_2 and pure **Ce-NCS** was obtained by recrystallization from methanol following washing. The isolated compound matched previously reported characterization data.

The presence of a single coordinated water molecule was confirmed by IR spectroscopy (Figure S-2) which revealed unique –OH stretches at 3433 and 3366 cm^{-1} for dry crystals of **Ce-NCS** which shifted to a broad signal at 2407 cm^{-1} when the synthesis was conducted in wet (10 μL D_2O added) deuterated methanol. This is consistent with the isotopic shift expected, and indicates water incorporation in the crystal lattice.

Previously reported diffraction data for **Ce-NCS** were solved in the space group Pm-3.[13b] The structure we obtained, however, contained the additional symmetry elements of the space group Pm-3m. For this reason, we elected to resolve the structure of **Ce-NCS** in Pm-3m.

Single Crystal X-ray Diffraction. Crystals were mounted on glass fibers and affixed using a quick drying epoxy. Full spheres of data were collected at 100 and 300 K on a Bruker Apex II diffractometer using Mo Kα radiation. The data were corrected for absorption using SADABS,[32] and the structure was solved using direct methods (SHELXS).[33] Structure refinement was carried out using SHELXL software. The methylene (CH_2) carbons of the Et_4N^+ cations in the structures of **Th-NCS** and **Pu-NCS** were disordered about a 2-fold ration axis through the central nitrogen atom. As both sites are crystallographically equivalent, the occupancy of these carbons was fixed at ½. **Ce-NCS** also displays similar behavior with the Et_4N^+ disordered about special positions. The occupancy of carbon atoms at these disordered sites was fixed so each atom had a total occupancy of one. The structure of **Ce-NCS** features seven coordinated thiocyanate ligands and a single coordinated water molecule. The water molecule was modeled as 1/8 occupancy across all eight ligand sites. Hydrogen atoms could not be located in the difference map, and a suitable combination of constraints could not be identified to assign hydrogen atoms in riding positions at the disordered cations. Hydrogen atoms were therefore omitted from the structure refinement for **Th-NCS**, **Pu-NCS** and **Ce-NCS**. For compound **Pu-OTf** (Figure S-9), hydrogen atoms attached to coordinated water molecules could not be identified in the difference map. For this reason, the hydrogen atoms were also omitted from this structure. CCDC 1412672, 1412675 (**Pu-NCS)**, 1412673, 1412676 (**Ce-NCS),** 1412671, 1412674 (**Th-NCS**), and 1412677 (**Pu-OTf**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray Diffraction. A slurry of **Pu-NCS** partially dissolved in acetone was prepared and several drops placed on an amorphous silicon plate. The acetone was allowed to evaporate and the plate was then covered with a Kapton window for radiological protection. Powder diffraction data were collected on a Scintag X1 diffractometer using Cu Kα radiation. Data were collected from 2θ = 5-120°. Acceptable signal to noise was only obtained out to 60° however. A stepsize of 0.1° was used with a total count time of 15 seconds at each step. A background was collected on an empty holder and subtracted from the data to remove a broad amorphous feature at low angles. The simulated powder pattern was generated using Mercury version 3.5.1 (Figure S-1).[34]

Raman Spectroscopy. Raman spectra were collected on randomly oriented single crystals utilizing a Renishaw inVia Raman microscope using circularly polarized light from a 532 or 785 nm diode laser. Radioactive samples were mounted on a glass drop-slide and covered with a glass coverslip affixed with epoxy. Data were collected from 100 to 4000 cm^{-1}. Plutonium samples proved highly susceptible to damage from laser irradiation. As such, spectra were collected at low laser power, and show a large glass luminesce feature (1,200-1,700 cm^{-1}) unrelated to the sample (Figure S-3).

UV-Vis Spectra. Spectra were collected on a Cary 14 spectrophotometer modernized by Olis Incorporated. Aqueous spectra were collected in 1 cm plastic cuvettes with a 240 nm cutoff. Specta in acetonitrile were collected in 0.2 cm quartz cuvettes. Spectra were collected in double beam mode against a solvent blank. The concentration of ^{242}Pu containing samples was determined by scintillation counting prior to spectral collection for the purpose of estimating molar absorbtivities.

Acknowledgements

This work was performed at Argonne National Laboratory, operated by UChicagoArgonne LLC for the United States Department of Energy under Contract DE-AC02-06CH11357, and was supported by a DOE Office of Basic Energy Sciences, Chemical Sciences, the Heavy Elements Program.

Keywords: Actinides, Coordination Chemistry, Plutonium, Thiocyanate

[1] R. M. Diamond, K. Street, G. T. Seaborg, *J. Am. Chem. Soc.* **1954**, *76*, 1461-1469.

[2] a) G. R. Choppin, *J. Less Common Metals* **1983**, *93*, 323-330; b) G. R. Choppin, *J. Alloys Compd.* **1995**, *223*, 174-179; c) G. R. Choppin, *J. Alloys Compd.* **2002**, *344*, 55-59; d) M. L. Neidig, D. L. Clark, R. L. Martin, *Coord. Chem. Rev.* **2013**, *257*, 394-406; e) S. G. Minasian, J. L. Krinsky, J. Arnold, *Chem. Eur. J.* **2011**, *17*, 12234-12245; f) M. P. Jensen, A. H. Bond, *J. Am. Chem. Soc.* **2002**, *124*, 9870-9877.

[3] a) A. E. V. Gorden, M. A. DeVore, B. A. Maynard, *Inorg. Chem.* **2013**, *52*, 3445-3458; b) Z. Szabó, T. Toraishi, V. Vallet, I. Grenthe, *Coord. Chem. Rev.* **2006**, *250*, 784-815; c) S. Krivovichev, P. Burns, I. Tananaev, *Structural Chemistry of Inorganic Actinide Compounds*, Elsevier Science, **2006**.

[4] F. L. Moore, *Anal. Chem.* **1964**, *36*, 2158-2162.

[5] a) M. J. Hudson, L. M. Harwood, D. M. Laventine, F. W. Lewis, *Inorg. Chem.* **2013**, *52*, 3414-3428; b) K. L. Nash, *Solvent Extr. Ion Exch.* **1993**, *11*, 729-768; c) M. P. Jensen, L. R. Morss, J. V. Beitz, D. D. Ensor, *J. Alloys Compd.* **2000**, *303–304*, 137-141; d) K. L. Nash, R. E. Barrans, R. Chiarizia, M. L. Dietz, M. P. Jensen, P. G. Rickert, B. A. Moyer, P. V. Bonnesen, J. C. Bryan, R. A. Sachleben, *Solvent Extr. Ion Exc.* **2000**, *18*, 605-631.

[6] a) R. J. Ellis, M. Audras, M. R. Antonio, *Langmuir* **2012**, *28*, 15498-15504; b) R. J. Ellis, Y. Meridiano, J. Muller, L. Berthon, P. Guilbaud, N. Zorz, M. R. Antonio, T. Demars, T. Zemb, *Chem. Eur. J.* **2014**, *20*, 12796-12807; c) B. Qiao, T. Demars, M. Olvera de la Cruz, R. J. Ellis, *J. Phys. Chem. Lett.* **2014**, *5*, 1440-1444.

[7] a) R. Chiarizia, P. R. Danesi, G. Scibona, L. Magon, *J. Inorg. Nuc. Chem.* **1973**, *35*, 3595-3604; b) R. Chiarizia, R. C. Gatrone, E. P. Horwitz, *Solvent Extr. Ion Exch.* **1995**, *13*, 615-645; c) G. R. Choppin, J. Ketels, *J. Inorg. Nucl. Chem.* **1965**, *27*, 1335-1339; d) P. K. Khopkar, J. N. Mathur, *J. Inorg. Nuc. Chem.* **1974**, *36*, 3819-3825; e) W. F. Kinard, G. R. Choppin, *J. Inorg. Nucl. Chem.* **1974**, *36*, 1131-1134.

[8] a) P. K. Khopkar, J. N. Mathur, *Thermochim. Acta* **1980**, *37*, 71-78; b) G. R. Choppin, *J. Alloys Compd.* **1997**, *249*, 9-13.

[9] J. N. Mathur, K. L. Nash, *Solvent Extr. Ion Exc.* **1998**, *16*, 1341-1356.

[10] a) A. Bahta, G. A. Parker, D. G. Tuck, in *Pure and Applied Chemistry, Vol. 69*, **1997**, p. 1489; b) R. J. Lemire, N. D. Bank, O. N. E. Agency, *Chemical Thermodynamics of Neptunium and Plutonium*, Elsevier, **2001**; c) P. K. Khopkar, P. Narayanankutty, *J. Inorg. Nuc. Chem.* **1971**, *33*, 495-502; d) P. K. Khopkar, J. N. Mathur, *J. Inorg. Nuc. Chem.* **1980**, *42*, 109-113.

[11] L. Soderholm, S. Skanthakumar, R. E. Wilson, *J. Phys. Chem. A* **2011**, *115*, 4959-4967.

[12] L. Soderholm, S. Skanthakumar, R. E. Wilson, *J. Phys. Chem. A* **2009**, *113*, 6391-6397.

[13] a) J. L. Martin, L. C. Thompson, L. J. Radonovich, M. D. Glick, *J. Am. Chem. Soc.* **1968**, *90*, 4493-4494; b) Y. Tateyama, Y. Kuniyasu, Y. Suzuki, A. Ouchi, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2805-2810; c) F. Matsumoto, N. Matsumura, A. Ouchi, *Bull. Chem. Soc. Japan* **1989**, *62*, 1809-1816; d) M. J. Lozano-Rodriguez, R. Copping, S. Petit, P. L. Solari, P. Guilbaud, J. Mustre de Leon, C. Den Auwer, *New Journal of Chemistry* **2011**, *35*, 2755-2765; e) B. Mallick, B. Balke, C. Felser, A.-V. Mudring, *Angewandte Chemie International Edition* **2008**, *47*, 7635-7638.

[14] M. Kabešová, J. Gažo, *Chem. Zvesti* **1980**, *34*, 800-841.

[15] a) P. Charpin, M. Lance, A. Navaza, *Acta. Cryst. Sec. C* **1983**, *39*, 190-192; b) R. Countryman, W. S. McDonald, *J. Inorg. Nuc. Chem.* **1971**, *33*, 2213-2220; c) W. P. Griffith, M. J. Mockford, *J. Chem. Soc. Dalton Trans.* **1986**, 1057-1058; d) E. Hashem, J. A. Platts, F. Hartl, G. Lorusso, M. Evangelisti, C. Schulzke, R. J. Baker, *Inorg. Chem.* **2014**, *53*, 8624-8637; e) C. E. Rowland, M. G. Kanatzidis, L. Soderholm, *Inorg. Chem.* **2012**, *51*, 11798-11804; f) Z. M. S. Al-Kazzaz, K. W. Bagnall, D. Brown, B. Whittaker, *J. Chem. Soc. Dalton Trans.* **1972**, 2273-2277; g) R. G. Surbella Iii, C. L. Cahill, *CrystEngComm* **2014**, *16*, 2352-2364; h) K. W. Bagnall, L. Xing-fu, G. Bombieri, F. Benetollo, *J. Chem. Soc. Dalton Trans.* **1982**, 19-23; i) D. L. Kepert, J. M. Patrick, A. H. White, *J. Chem. Soc. Dalton Trans.* **1983**, 559-566; j) N. Aoyagi, K. Shimojo, N. R. Brooks, R. Nagaishi, H. Naganawa, K. V. Hecke, L. V. Meervelt, K. Binnemans, T. Kimura, *Chemical Communications* **2011**, *47*, 4490-4492; k) R. O. Wiley, R. B. Von Dreele, T. M. Brown, *Inorg. Chem.* **1980**, *19*, 3351-3356; l) E. Hashem, G. Lorusso, M. Evangelisti, T. McCabe, C. Schulzke, J. A. Platts, R. J. Baker, *Dalton Trans.* **2013**, *42*, 14677-14680.

[16] a) N. A. Budantseva, G. B. Andreev, A. M. Fedoseev, M. Y. Antipin, *Radiochemistry* **2003**, *45*, 335-338; b) P. R. Vasudeva Rao, S. V. Bagawde, V. V. Ramakrishna, S. K. Patil, *J. Inorg. Nuc. Chem.* **1978**, *40*, 339-343.

[17] a) M. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions*, National Association of Corrosion Engineers, **1974**; b) A. J. Bard, R. Parsons, J. Jordan, *Standard Potentials in Aqueous Solution*, Taylor & Francis, **1985**; c) D. Cohen, *J. Inorg. Nuc. Chem.* **1961**, *18*, 211-218.

[18] R. E. Wilson, P. M. Almond, P. C. Burns, L. Soderholm, *Inorg. Chem.* **2006**, *45*, 8483-8485.

[19] a) J. A. Davies, *Synthetic Coordination Chemistry: Principles and Practice*, World Scientific, **1996**; b) J. H. Matonic, B. L. Scott, M. P. Neu, *Inorg. Chem.* **2001**, *40*, 2638-2639; c) C. Apostolidis, B. Schimmelpfennig, N. Magnani, P. Lindqvist-Reis, O. Walter, R. Sykora, A. Morgenstern, E. Colineau, R. Caciuffo, R. Klenze, R. G. Haire, J. Rebizant, F. Bruchertseifer, T. Fanghänel, *Angewandte Chemie* **2010**, *122*, 6487-6491; d) S. Skanthakumar, M. R. Antonio, R. E. Wilson, L. Soderholm, *Inorg. Chem.* **2007**, *46*, 3485-3491; e) J. Harrowfield, D. Kepert, J. Patrick, A. White, *Australian Journal of Chemistry* **1983**, *36*, 483-492; f) C. Cossey, D. H. Powell, L. Helm, A. E. Merbach, *New Journal of Chemistry* **1995**, *19*, 27.

[20] a) P. Di Bernardo, G. R. Choppin, R. Portanova, P. L. Zanonato, *Inorganica chimica acta* **1993**, *207*, 85-91; b) A. M. van Loon, H. van Bekkum, J. A. Peters, *Inorg. Chem.* **1999**, *38*, 3080-3084; c) A.-V. Mudring, A. Babai, S. Arenz, R. Giernoth, *Angewandte Chemie International Edition* **2005**, *44*, 5485-5488; d) S. Tang, A. Babai, A.-V. Mudring, *Angewandte Chemie International Edition* **2008**, *47*, 7631-7634.

[21] Note that thiocyanate (pKa ~1) is predominantly protonated in 1 M HCl.

[22] a) G. H. Coleman, *The Radiochemistry of Plutonium*, Subcommittee on Radiochemistry, National Accademy of Sciences-National Research Council; available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., **1965**; b) W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, Prentice-Hall, **1959**.

[23] Charpin and Lance noted that both a cubic and tetragonal phase can be obtained for Th-NCS dependent on the conditions utilized in the synthesis.

[24] a) F. A. Cotton, G. Wilkinson, *Advanced inorganic chemistry*, John Wiley & Sons, Incorporated, **1988**; b) T. A. Albright, J. K. Burdett, M. H. Whangbo, *Orbital interactions in chemistry*, Wiley, **1985**; c) R. L. DeKock, H. B. Gray, *Chemical Structure and Bonding*, University Science Books, **1989**.

[25] R. Shannon, *Acta Cryst. Sec. A* **1976**, *32*, 751-767.

[26] a) L. R. Morss, N. M. Edelstein, J. Fuger, *The Chemistry of the Actinide and Transactinide Elements (Set Vol.1-6): Volumes 1-6*, Springer, **2010**; b) G. N. Lewis, *Valence and the structure of atoms and molecules*, The Chemical Catalog Company, inc., **1923**.

[27] J. R. Ferraro, *Low-Frequency Vibrations of Inorganic and Coordination Compounds*, Springer US, **2012**.

[28] K. Nakamoto, in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, Inc., **2008**, pp. 1-147.

[29] Note that reduced mass of the Ce-N bond is 96% of that for 242Pu-N

[30] a) F. A. Cotton, *CHEMICAL APPLICATIONS OF GROUP THEORY, 3RD ED*, Wiley India, **2008**; b) S. F. A. Kettle, *Symmetry and Structure: Readable Group Theory for Chemists*, Wiley, **2008**.

[31] J. J. Barnett, M. L. McKee, D. M. Stanbury, *Inorg. Chem.* **2004**, *43*, 5021-5033.

[32] Bruker APEX2 Sortware Suite, APEX2 v2011.4-1; Bruker AXS: Madison, WI, 2011.

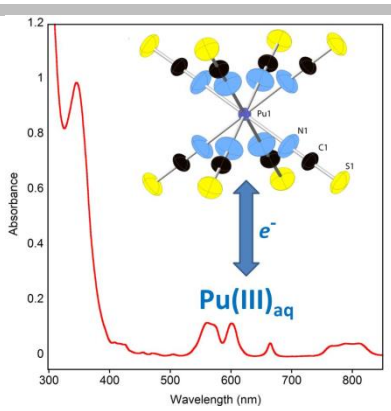
[33] Sheldrick, G. M. SHELXTL; Bruker AXS, Madison, WI, 1997.

[34] Mercury CSD 2.0 - New Features for the Visualization and Investigation of Crystal Structures C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, J. Appl. Cryst., 41, 466-470, 2008

Entry for the Table of Contents

FULL PAPER

Plutonium (III and IV) coordination chemistry with thiocyanate is examined and compared to other tetravalent actinides, and Ce(III), to study fundamental chemical differences among the 5*f* and 4*f* elements. While no thiocyanate-Pu(III) interaction was observed in solution or the solid state, spectroscopic investigations reveal enhanced interactions with the An(IV) ions and weaker interactions with the trivalent lanthanide Ce.



*Tyler J. Carter, Richard E. Wilson**

Page No. – Page No.

Coordination chemistry of homoleptic actinide(IV) thiocyanate complexes