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SHORT COMMUNICATION

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The Homoleptic $\text{U}(\text{NCSe})_8^{4-}$ Anion in $(\text{Pr}_4\text{N})_4\text{U}(\text{NCSe})_8 \cdot 2\text{CFCl}_3$ and $\text{Th}(\text{NCSe})_4(\text{OP}(\text{NMe}_2)_3)_4 \cdot 0.5\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$: First Structurally Characterized Actinide Isoselenocyanates

Margaret-Jane Crawford,* Konstantin Karaghiosoff and Peter Mayer

Keywords: Thorium ; Uranium ; Pseudohalides ; Structure elucidation; Isoselenocyanates

The neutral thorium complex $\text{Th}(\text{NCSe})_4(\text{OP}(\text{NMe}_2)_3)_4$ and homoleptic octa(isoselenocyanato)uranate anion $\text{U}(\text{NCSe})_8^{4-}$ in $(\text{Pr}_4\text{N})_4\text{U}(\text{NCSe})_8 \cdot 2\text{CFCl}_3$ were synthesized and structurally characterized. $(\text{Pr}_4\text{N})_4\text{U}(\text{NCSe})_8 \cdot 2\text{CFCl}_3$ contains the U(IV) anion $\text{U}(\text{NCSe})_8^{4-}$ and was characterized using IR spectroscopy and single crystal X-ray diffraction. $\text{Th}(\text{NCSe})_4(\text{OP}(\text{N}(\text{CH}_3)_2)_3)_4 \cdot 0.5\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ was characterized using IR and Raman

spectroscopy, as well as $^{31}\text{P}\{^1\text{H}\}$, $^{15}\text{N}\{^1\text{H}\}$, $^{14}\text{N}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, ^1H and ^{77}Se NMR spectroscopy and structurally characterized using single crystal X-ray diffraction. The $\text{U}(\text{NCSe})_8^{4-}$ anion and $\text{Th}(\text{NCSe})_4(\text{OP}(\text{N}(\text{CH}_3)_2)_3)_4 \cdot 0.5\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ complex are the first structurally characterized actinide-isoselenocyanates. The crystal structures shows an approximate square antiprism arrangement of the ligands around the actinide(IV) centres.

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Introduction

Relatively few pseudohalide complexes of the actinides have been unambiguously characterised, and even fewer homoleptic actinide pseudohalide complexes have been reported in the literature.^[1] The number of structurally characterised thorium pseudohalide complexes is considerably smaller, and is limited to only thorium isothiocyanates.^[2] To the best of our knowledge, no other classes of thorium pseudohalide complexes have been investigated structurally. The existing literature reports of structurally characterised homoleptic actinide pseudohalides consists of five salts containing actinide isothiocyanate anions, namely, $\text{Cs}_4\text{U}(\text{NCS})_8$,^[3a] $(\text{Et}_4\text{N})_4\text{U}(\text{NCS})_8$,^[3b] $(\text{Et}_4\text{N})_4\text{Th}(\text{NCS})_8$ ^[2a] and $(\text{Me}_4\text{N})_4\text{Np}(\text{NCS})_8$ ^[3c] as well as the recently reported heptaazidouranate(IV) anion in $(\text{Bu}_4\text{N})_3\text{U}(\text{N}_3)_7$.^[4] To the best of our knowledge, although actinide isoselenocyanates have been previously reported in the literature,^[5] and several uranium(IV), uranium(VI) and thorium(IV) complexes have been prepared and spectroscopically characterised including $\text{Th}(\text{NCSe})_4(\text{OP}(\text{NMe}_2)_3)_4$,^[5a] none have been unambiguously identified and structurally characterised. The synthesis and preliminary crystallographic data has been reported for $(\text{Et}_4\text{N})_4\text{U}(\text{NCSe})_8$ ^[5i], $(\text{Et}_4\text{N})_4\text{Pa}(\text{NCSe})_8$ ^[5ii] and $(\text{Et}_4\text{N})\text{U}(\text{NCSe})_5(\text{bipy})_2$ ^[5d] however, the geometry and structural parameters of the $\text{U}(\text{NCSe})_8^{4-}$, $\text{Pa}(\text{NCSe})_8^{4-}$ and $\text{U}(\text{NCSe})_5(\text{bipy})_2^-$ anions were not reported.

Results and Discussion

The synthesis of **(1)** followed a similar route to that used for the synthesis of $(\text{Bu}_4\text{N})_3\text{U}(\text{N}_3)_7$ ^[4], or $(\text{Et}_4\text{N})_4\text{U}(\text{NCS})_8$ ^[6], whereby $(\text{Pr}_4\text{N})_2\text{UCl}_6$ was reacted with two equivalents of Pr_4NCl and eight equivalents of KSeCN in acetonitrile at room temperature. On recrystallisation from a $\text{CH}_3\text{CN}/\text{CFCl}_3$ mixture, a very small quantity of very small emerald green/yellow air sensitive crystals of $(\text{Pr}_4\text{N})_4\text{U}(\text{NCSe})_8 \cdot 2\text{CFCl}_3$ formed. On leaving the green solution in air, red or grey selenium was observed to precipitate within hours. The green solid was indefinitely stable at room temperature when stored under an inert atmosphere in the dark. The solid state IR spectrum of $(\text{Pr}_4\text{N})_4\text{U}(\text{NCSe})_8$ was tentatively assigned based on the previous assignments by *Bailey et al.* and others for $(\text{Cs}_4\text{U}(\text{NCSe})_8$ ^[7a,b] and *Chatt and Duncanson* for the homoleptic transition metal isoselenocyanates ($n\text{-Bu}_4\text{N})_4\text{M}(\text{NCSe})_8$ ($\text{M} = \text{Mn}, \text{Ni}$) and $(n\text{-Bu}_4\text{N})_2\text{Fe}(\text{NCSe})_4$ ^[7c,d]. In the IR spectrum of **(1)**, several bands were observed for the Pr_4N^+ cations, as well as the $\nu(\text{CN})$ vibrations which were observed at 2093 and 2054 cm^{-1} . The presence of more than one $\nu(\text{CN})$ vibration in the IR spectrum of compound **(1)** is in good agreement with the observations of *Bombieri et al.* for $\text{Cs}_4\text{U}(\text{NCS})_8$ ^[3a], where the $\text{U}(\text{NCS})_8^{4-}$ anion adopts a square antiprism arrangement of the eight SCN^- ligands. The $\text{U}(\text{NCSe})_8^{4-}$ anion in **1** shows an approximate square antiprism arrangement of the eight N atoms of the SeCN ligands around the U(IV) centre, similar to the geometry observed previously for the $\text{U}(\text{NCS})_8^{4-}$ anion in $\text{Cs}_4\text{U}(\text{NCS})_8$ ^[3a] with essentially identical U-N bond lengths ($d(\text{U-N}) = 2.441(6) - 2.446(6) \text{ \AA}$) (Figure 1) similar to those observed in $\text{Cs}_4\text{U}(\text{NCS})_8$ ($d(\text{U-N}) = 2.38(3) - 2.46(3) \text{ \AA}$).^[3a] The $d(\text{N-C})$ and $d(\text{C-Se})$ bond lengths in the $\text{U}(\text{NCSe})_8^{4-}$ anion ($1.153(8) - 1.162(8) \text{ \AA}$, and $1.771(7) - 1.784(7) \text{ \AA}$ respectively), are comparable with the related transition metal isoselenocyanate complex $(\text{Bu}_4\text{N})_3\text{Cr}(\text{NCSe})_6$ ($d(\text{N-C})_{\text{average}} = 1.125 \text{ \AA}$; $d(\text{C-Se})_{\text{average}} = 1.794 \text{ \AA}$)^[8] and show a slight shortening of the Se-C bond, in

comparison with that observed in KSeCN ($d(\text{N}-\text{C}) = 1.117 \pm 0.026 \text{ \AA}$; $d(\text{C}-\text{Se}) = 1.829 \pm 0.025 \text{ \AA}$)^[9]. Although the isoselenocyanate ligand is an ambidentate ligand, all of the SeCN^- ligands are coordinated to the U(IV) centre via nitrogen and show three similar $\angle(\text{U}-\text{N}-\text{C})$ angles of $165.6(5)$, $168.0(5)$ and $169.9(5)^\circ$, as well as one considerably smaller $\angle(\text{U}-\text{N}-\text{C})$ angle of $156.1(6)^\circ$. In addition, two disordered CFCl_3 solvent molecules are present. The $\text{U}(\text{NCSe})_8^{4-}$ anion however, shows slight distortions from the ideal square antiprism geometry with D_{4d} symmetry. Even although uranium can display high coordination numbers, there are relatively few structurally characterised homoleptic uranium complexes containing monodentate ligands, where the central uranium atom has a coordination number of eight.

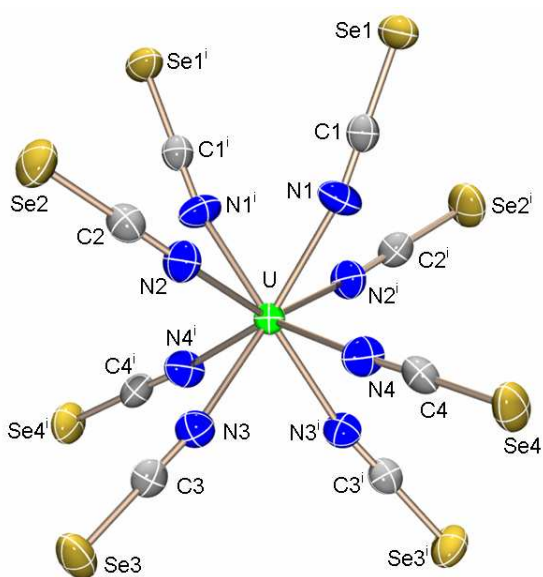


Figure 1. Molecular structure of the $\text{U}(\text{NCSe})_8^{4-}$ anion in $(\text{Pr}_4\text{N})_4\text{U}(\text{NCSe})_8\cdot 2\text{CFCl}_3$ (**1**) as determined using single crystal X-ray diffraction with thermal ellipsoids shown at the 50 % probability level; $i = 1-x, y, 1-z$. Selected bond lengths [\AA] and angles [$^\circ$]: U-N1 2.444(6), U-N2 2.441(6), U-N3 2.446(6), U-N4 2.442(6), N1-C1 1.158(8), N2-C2 1.162(8), N3-C3 1.153(8), N4-C4 1.160(9), C1-Se1 1.774(7), C2-Se2 1.776(7), C3-Se3 1.784(7), C4-Se4 1.771(7), U1-N1-C1 165.6(5), U1-N2-C2 156.1(6), U1-N3-C3 169.9(5), U1-N4-C4 168.0(5), N1-C1-Se1 179.7(9), N2-C2-Se2 179.2(7), N3-C3-Se3 179.2(7), N4-C4-Se4 178.6(6), N1-U-N2 76.3(2), N2-U-N3 72.0(2), N3-U-N4 79.2 (2), N4-U-N1 72.4(2).

To the best of our knowledge, the only thorium pseudohalide complexes which have been structurally characterised using single crystal X-ray diffraction are $\text{Th}(\text{NCS})_4\text{L}_4$ ($\text{L} = \text{OP}(\text{NMe}_2)_3$ ^[2b]; $\text{OC}(\text{Et})\text{NMe}_2$ ^[2d]; $\text{OC}(\text{NMe}_2)_2$ ^[2c]; $\text{OC}(\text{Me})\text{N}^i\text{Pr}_2$ ^[3b]), $(\text{Et}_4\text{N})_4\text{Th}(\text{NCS})_8$ ^[2a], $\text{Th}(\text{NCS})_4(\text{OC}(\text{Pr})\text{N}^i\text{Pr}_2)_3$ ^[2f] and

$\text{Th}(\text{NCS})_2\text{Cl}_2(\text{OC}(\text{Me})\text{N}(\text{C}_6\text{H}_{11})_2)_3$ ^[2f]. All of the compounds listed above contain the isothiocyanate (NCS^-) pseudohalide, and to the best of our knowledge, no thorium complex containing any other member of the pseudohalides has been structurally characterised using single crystal X-ray diffraction. The synthesis of $\text{Th}(\text{NCSe})_4(\text{OP}(\text{NMe}_2)_3)_4\cdot 0.5\text{CH}_3\text{CN}\cdot 0.5\text{H}_2\text{O}$ (**2**) occurred via the reaction of $\text{Th}(\text{NO}_3)_4\cdot 5\text{H}_2\text{O}$ with $\text{OP}(\text{NMe}_2)_3$, followed by the addition of KSeCN . Colourless crystals of the air sensitive complex (**2**) were obtained by concentrating the filtrate and cooling the saturated solution to 4°C . The large colourless crystals that subsequently formed were characterised using IR and Raman spectroscopy, as well as ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{14/15}\text{N}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and ^{77}Se NMR spectroscopy, in addition to single crystal X-ray diffraction. The tentative assignments of the vibrational spectra of compound (**2**) in the range $4000 - 700 \text{ cm}^{-1}$ were made based on the assignments in the literature for the free $\text{OP}(\text{NMe}_2)_3$ ligand,^[10] $\text{Th}(\text{NCS})_4(\text{OP}(\text{NMe}_2)_3)_4$ ^[11] and $(n\text{-Bu}_4\text{N})_4\text{M}(\text{NCSe})_6$ ($\text{M} = \text{Mn}, \text{Ni}$).^[7c,d] However, due to the low intensity of the Th-N stretch in (**2**), it has not been assigned. The presence of the SeCN ligands in (**2**) could be clearly observed in the $^{13}\text{C}\{^1\text{H}\}$ (126.3 ppm), $^{14}\text{N}\{^1\text{H}\}$ (-136 ppm), $^{15}\text{N}\{^1\text{H}\}$ (-136.2 ppm) and ^{77}Se (-316 ppm) NMR spectra, with chemical shifts similar to those of KSeCN (^{13}C (119.2 ppm), ^{14}N (-138 ppm) and ^{77}Se (-330 ppm)).^[12] For the $\text{OP}(\text{NMe}_2)_3$ ligand, signals at 2.77 (^1H NMR), 36.9 (^{13}C NMR), 27.1 ($^{31}\text{P}\{^1\text{H}\}$ NMR) and -357.1 ppm ($^{15}\text{N}\{^1\text{H}\}$ NMR) were observed. The single crystal structure of (**2**) again shows a distorted approximate square antiprism arrangement of the eight coordinated ligands consisting of the four N atoms of the SeCN ligands and four O atoms of the $\text{OP}(\text{NMe}_2)_3$ ligands. (Figure 2)

Each square face contains two nitrogen and two oxygen atoms in *trans* positions, and when viewed from above, the ligands alternate within one square face. The second square face also shows this arrangement, however since the two faces are rotated with respect to each other, the ligands do not alternate when viewed from above. The Th-N bond lengths in the two crystallographically independent molecules of (**2**) ($d(\text{Th}-\text{N}) = 2.513(8), 2.559(8), 2.515(8), 2.558(8) \text{ \AA}$) are similar to those reported for $\text{Th}(\text{NCS})_4(\text{OC}(\text{NMe}_2)_2)_4$ ($d(\text{Th}-\text{N}) = 2.50(1), 2.52(1)$ and $2.54(1) \text{ \AA}$),^[2c] and are significantly shorter than those reported in the crystal structure of $\text{ThCl}_4(\text{NMe}_2)_3$ ($d(\text{Th}-\text{N}) = 2.787(29), 2.83(3), 2.66(4) \text{ \AA}$), which contains neutral trimethylamine Lewis base ligands coordinated to the Th(IV) centre.^[13] The Se-C and N-C bond lengths in (**1**) and (**2**) are similar, and the An-N bond lengths (An = Actinide) observed in (**2**) are longer than those observed in (**1**). It is worthwhile to mention that the $\angle(\text{Th}-\text{N}-\text{C})$ angles in $\text{Th}(\text{NCS})_4(\text{OC}(\text{NMe}_2)_2)_4$ show a wide range of values ($\angle(\text{Th}-\text{N}-\text{C}) = 155.4(1.2) - 175.0(1.2)^\circ$)^[2c] as was observed for both compounds (**1**) and (**2**). However, the $\angle(\text{N}-\text{C}-\text{X})$ ($\text{X} = \text{S}, \text{Se}$) angles in $\text{Th}(\text{NCS})_4(\text{OC}(\text{NMe}_2)_2)_4$, (**1**) and (**2**) deviate only slightly from linearity.

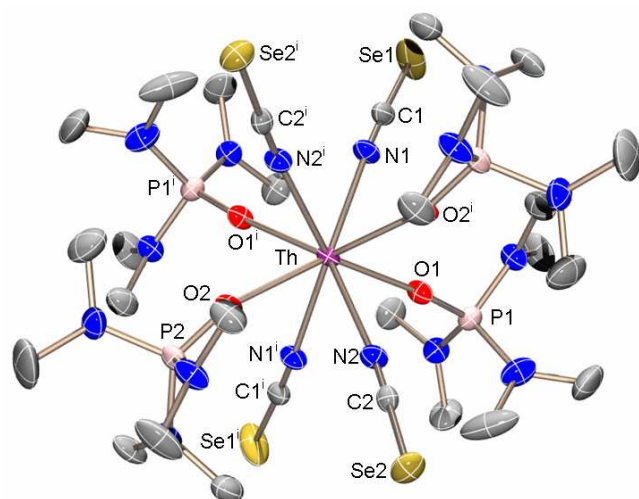


Figure 2. Molecular structure of one of the crystallographically independent $\text{Th}(\text{NCSe})_4(\text{OP}(\text{N}(\text{CH}_3)_2)_3)_4$ molecules in **(2)** as determined using single crystal X-ray diffraction with thermal ellipsoids shown at the 25 % probability level; $i = \frac{1}{2} - x, y, -z$. Hydrogen atoms are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Th1-N1 2.513(8), Th1-N2 2.559(8), N1-C1 1.151(12), N2-C2 1.151(11), C1-Se1 1.788(12), C2-Se2 1.784(10), Th1-O1 2.350(6), Th1-O2 2.381(6), O1-P1 1.497(6), O2-P2 1.495(6), Th1-N1-C1 167.6(8), Th1-N2-C2 167.0(7), N1-C1-Se1 177.5(10), N2-C2-Se2 178.8(9), Th1-O1-P1 173.9(4), Th1-O2-P2 163.8(4), N1-Th1-N2 142.1(3).

Although both **(1)** and **(2)** are stable in the solid state in the dark at room temperature, they are air and moisture sensitive. While **(1)** decomposes rapidly in the presence of moisture, **(2)** was found to decompose slowly. The synthesis of further complexes, particularly of thorium is required, in order to understand better the chemistry of this poorly investigated element. A further interesting aspect of actinide chemistry is the increasing use of DFT methods to investigate more comprehensively the bonding in actinide compounds.^[14] Therefore, the synthesis and structure determination of simple complexes of thorium is of added interest, to provide experimentally determined structural data for comparison with computational results. DFT calculations may then be a useful technique to predict possible new synthetic target compounds.

Conclusions

The first structurally characterized actinide isoselenocyanate complexes have been reported in the compounds $(\text{Pr}_4\text{N})_4\text{U}(\text{NCSe})_8 \cdot 2\text{CFCl}_3$ containing U(IV) and $\text{Th}(\text{NCSe})_4(\text{OP}(\text{N}(\text{CH}_3)_2)_3)_4 \cdot 0.5\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ containing Th(IV). Both the $\text{U}(\text{NCSe})_8^{4-}$ anion and $\text{Th}(\text{NCSe})_4(\text{OP}(\text{N}(\text{CH}_3)_2)_3)_4$ moiety show a square antiprismatic arrangement of the eight ligands around the central An(IV) atom (An = U, Th). Both compounds are air sensitive.

Experimental Section

$(\text{Pr}_4\text{N})_2\text{UCl}_6$ was prepared according to literature procedures.^[15] Pr_4NBr (Fluka), $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (Merck), KSeCN (Aldrich) and CFCl_3 (Merck) were used as received. CH_3CN (Merck) and

$\text{CH}_3\text{CH}_2\text{CN}$ (Aldrich) were dried over P_4O_{10} and distilled immediately prior to use. IR spectra of $(\text{Pr}_4\text{N})_4\text{U}(\text{NCSe})_8$ and $\text{Th}(\text{NCSe})_4(\text{OP}(\text{NMe}_2)_3)_4$ were recorded of the solid products between KBr plates. The samples were prepared in a nitrogen atmosphere glove-box and were recorded using a Perkin Elmer FT-IR Spectrum One spectrometer. Raman spectra were recorded of solids sealed under a nitrogen atmosphere in glass tubes at room temperature using a Perkin-Elmer 2000 NIR FT-Raman spectrometer fitted with a Nd:YAG laser (1064 nm). Multinuclear NMR spectra were recorded using a Jeol eclipse 400 spectrometer and chemical shifts referenced to Me_4Si (^1H , ^{13}C), MeNO_2 (^{14}N), 85% H_3PO_4 (^{31}P) and Me_2Se (^{77}Se) as external standards. **Caution ! All uranium and thorium compounds, and in particular $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, should be handled with caution since both are radioactive and toxic.** Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Centre (CCDC, 12 Unions Road, Cambridge CB21EZ (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk)), on quoting the depository numbers CCDC-648986 and 648987.

Synthesis of $(\text{Pr}_4\text{N})_4\text{U}(\text{NCSe})_8 \cdot 2\text{CFCl}_3$: 0.211 g $(\text{Pr}_4\text{N})_2\text{UCl}_6$ (0.256 mmol), 0.136 g Pr_4NBr (0.512 mmol) and a magnetic stirrer bar were placed into a 25 mL Schlenk flask under a nitrogen atmosphere. Under a strong nitrogen purge, 10 mL freshly dried and distilled CH_3CN were added, and a clear pale green solution formed. Under a nitrogen flow, 0.295 g (2.048 mmol) of KSeCN were added, and the solution immediately turned emerald green. The reaction mixture was allowed to stir in the dark for 1 hour, after which time the volume of the solvent was reduced to approximately half, and then the solution decanted under a nitrogen atmosphere. To the concentrated green solution, enough CFCl_3 was added under a strong nitrogen purge to result in the precipitation of a very small quantity of very small emerald green crystals. The solution was decanted off, leaving behind the green crystals. The IR spectrum was recorded of an amorphous green powder formed after grinding the crystals and leaving under dynamic vacuum for 2 hours.

IR spectrum (RT, KBr plates, res. = 4 cm^{-1}): 2968m, 2933m, 2877w ($(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}^+$); 2093w 2054s, ($\nu(\text{CN})$); 1482 m, 1470m, 1457m, 1384m, 1326w, 1311w, 1241w, 1154w, 1057w, 1004vw, 986w, 967m, 931vw, 904w, 872w, 832m, 755m ($(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}^+$); 633m. Crystal data for $(\text{Pr}_4\text{N})_4\text{U}(\text{NCSe})_8 \cdot 2\text{CFCl}_3$ recrystallized from $\text{CH}_3\text{CN}/\text{CFCl}_3$ mixture: $\text{C}_{58}\text{H}_{112}\text{Cl}_6\text{F}_2\text{N}_{12}\text{Se}_8\text{U}_1$, Fwt. = 2098.01, yellow block, crystal size, 0.10 x 0.15 x 0.18 mm, monoclinic, space group $C2$, $a = 20.5959(3) \text{ \AA}$, $b = 17.0497(4) \text{ \AA}$, $c = 13.6951(3) \text{ \AA}$, $\beta = 115.169(1)^\circ$, $V = 4352.5(2) \text{ \AA}^3$, $Z = 2$, $\rho = 1.601 \text{ g cm}^{-3}$, $T = 200 \text{ K}$, $\mu = 5.437 \text{ mm}^{-1}$, $F(000) = 2056$, Nonius Kappa CCD diffractometer, $\text{Mo-K}\alpha$, $\lambda = 0.71073 \text{ \AA}$, Θ range = 3.2 to 25.1° , $-24 \leq h \leq 24$, $-20 \leq k \leq 20$, $-16 \leq l \leq 16$, reflections collected: 24071, independent reflections: 7637 ($R_{\text{int}} = 0.060$), observed reflections: 7114, structure solution: direct methods, SHELXS-97, $R_1[I > 2\sigma(I)] = 0.0364$, Final wR_2 (all data) = 0.0811, $S = 1.02$.

Synthesis of $\text{Th}(\text{NCSe})_4(\text{OP}(\text{NMe}_2)_3)_4$: 0.285 g $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (0.5 mmol) and a magnetic stirrer bar were placed into a 25 mL Schlenk flask under a nitrogen atmosphere. Under a strong nitrogen purge, 15 mL freshly dried and distilled CH_3CN were added, and a colourless solution formed. Under a nitrogen flow, 0.18 mL (1.0 mmol) $\text{OP}(\text{NMe}_2)_3$ were added using a syringe and the reaction mixture was left stirring at room temperature for 30 minutes. The volatile material was removed under reduced pressure at room temperature leaving a white solid, which was then re-

dissolved in 15 mL CH₃CN. Under a nitrogen purge, 0.288 (2.0 mmol) of solid KSeCN was then added and the resulting pale pink solution over a white insoluble solid was left stirring in the dark overnight. The volume of the filtrate was then reduced until a saturated solution was formed, and the reaction mixture was then left at 4°C for several days, after which time, large colourless crystals formed. The crystals were isolated, stored under an N₂ atmosphere and used for characterisation.

IR spectrum (RT, KBr plates, res. = 4 cm⁻¹, ν/cm⁻¹): 3433w, br (H₂O); 2994vw, 2923vw, 2898m, 2853m, 2810m (ν(NCH₃), OP(NMe₂)₃); 2054vs (ν(CN), NCSe); 1484m, 1453m (δ(NCH₃), OP(NMe₂)₃); 1305m (ρ_s(NCH₃), OP(NMe₂)₃); 1189m, 1080s; 993s (ν_s(NC₂), OP(NMe₂)₃); 758s (ν_{as}(PN), OP(NMe₂)₃); 644vw, 625w, 504vw, 478m. Raman spectrum (RT, 5 mm glass tube, res. = 4 cm⁻¹, ν/cm⁻¹): 3009(2), 2987(2), 2935(5), 2857(4), 2809(3) (ν(NCH₃), OP(NMe₂)₃); 2251(1) (ν(CN), CH₃CN); 2074(9), 2057(10), 2049(5) (ν(CN), NCSe); 1486(2), 1445(3), 1417(1) (δ(NCH₃), OP(NMe₂)₃); 1309(1) (ρ_s(NCH₃), OP(NMe₂)₃); 1140(1), 1080(1), 1051(1); 995(1) (ν_s(NC₂), OP(NMe₂)₃); 758(1) (ν_{as}(PN), OP(NMe₂)₃); 653(6) (ν_s(PN), OP(NMe₂)₃); 632(2), 510(2), 480(1), 382(2), 358(1). ³¹P{¹H} NMR (CDCl₃, 25°C): δ = 27.1 ppm (s, OP(NMe₂)₃); ¹⁵N{¹H} NMR (CDCl₃, 25°C): δ = -136.2 (s, NCSe), -357.1 (d, ¹J_{PN} = 38.4 Hz, OP(NMe₂)₃); ¹⁴N{¹H} NMR (CDCl₃, 25°C): δ = -136 (s, ν_{1/2} = 197 Hz, NCSe); ¹³C{¹H} NMR (CDCl₃, 25°C): δ = 126.3 ppm (s, NCSe), 36.9 (d, ²J_{PC} = 5.0 Hz, OP(N(CH₃)₂)₃), 1.9 (s, CH₃CN), 116.3 (s, CH₃CN); ¹H NMR (CDCl₃, 25°C): δ = 2.77 ppm (d, ³J_{PH} = 9.80 Hz, OP(N(CH₃)₂)₃), 1.97 (s, CH₃CN), 1.65 (s, br, H₂O); ⁷⁷Se NMR (CDCl₃, 25°C): δ = -316 ppm (s, NCSe). Crystal data for Th(NCSe)₄(OP(N(CH₃)₂)₃)₄·0.5CH₃CN·0.5H₂O recrystallized from CH₃CN: C₂₉H_{74.5}N_{16.5}O_{4.5}P₄Se₄Th₁, Fwt. = 1398.28, colourless block, crystal size, 0.30 x 0.25 x 0.19 mm, orthorhombic, space group I/bca, a = 23.3552(5) Å, b = 23.3882(5) Å, c = 41.6082(7) Å, V = 22708.4(8) Å³, Z = 16, ρ = 1.636 g cm⁻³; T = 100 K, μ = 5.350 mm⁻¹, F(000) = 10976, Oxford diffraction X-calibur S diffractometer, Mo-K_α = 0.71073 Å, θ range = 3.8 – 23.0°, -30 ≤ h ≤ 30, -30 ≤ k ≤ 30, -54 ≤ l ≤ 54, reflections collected: 85226, independent reflections: 7916 (R_{int} = 0.071), observed reflections: 7838, structure solution; direct methods, SHELXS-97, R1[I > 2σ(I)] = 0.0700, Final wR2 (all data) = 0.1190, Goof = 1.309.

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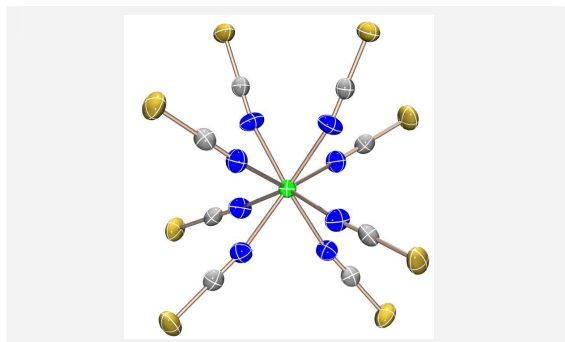
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