SUPPORTING INFORMATION

Activation of elemental S, Se, and Te with uranium(III): Bridging U–E–U (E = S, Se) and diamond-core complexes U–E_2–U (E = O, S, Se, Te)

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Abstract. Trivalent uranium complexes supported by tris(aryloxide) chelating ligands, $[((^{t\text{-Bu}}ArO)_3tacn)U]$ and $[((^{Ad}ArO)_3N)U]$, undergo activation of sulfur and selenium in their elemental forms, generating the mid-valent U(IV)(U(IV) complexes of the type $[\{((^{t\text{-Bu}}ArO)_3tacn)U\}_2(\mu\text{-E})]$ and $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-E})]$ (E = S, Se). Under reducing conditions, $[((^{Ad}ArO)_3N)U]$ reacts with elemental sulfur, selenium, and tellurium to yield the mid-valent dinuclear bis-μ-chalcogenide complexes $[Na(DME)_3]_2[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-E})_2]$ (E = S, Se, Te) with the diamond core structural motif and rare inorganic chalcogenide bridging ligands. For comparison, a unique high-valent U(V)/U(V) dinuclear complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-O})_2]$ was also synthesized. A short uranium-uranium distance in this complex with a $U(\mu\text{-O})_2U$ diamond core may account for the unusual temperature-dependent magnetic behavior.

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X-Ray Crystal Structure Data

Crystallographic Details for 3

Orange-red block-shaped crystals, grown from diffusion of hexane into a saturated solution of **3** in benzene at room temperature, were coated with isobutylene oil on a microscope slide. A crystal of approximate dimensions 0.10 × 0.10 × 0.05 mm^3 was selected and mounted on a nylon loop. A total of 55998 reflections ($-21 \leq h \leq 21$, $-22 \leq k \leq 21$, $-105 \leq l \leq 103$) were collected at T = 100(2) K in the θ range from 2.98 to 27.10º, of which 5180 were unique (R_{int} = 0.1414) and 2967 were observed [$I > 2\sigma(I)$] on a Bruker-Smart diffractometer using Mo$K\alpha$ radiation (λ = 0.71073 Å, graphite monochromator). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12, Bruker AXS, Inc., 2002). All non-hydrogen atoms were refined anisotropically. The dinuclear complex is situated on a crystallographic three-fold inversion axis (Wyckoff position 6*b*). The compound crystallizes with a total of three benzene and two hexane molecules per formula unit. The benzene is situated on a crystallographic two-fold axis (Wyckoff position 18*e*) while the hexane is disordered on a crystallographic three-fold axis (Wyckoff position 12*c*). The positional parameters of this disordered hexane were kept fixed during the refinement and no hydrogen atoms were included. All other hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron density were 2.413 and –2.426 e.$Å^{-3}$. The absorption coefficient was 2.360 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.1182, wR_2 = 0.1305, and GOF = 1.364 (all data). $C_{132}H_{202}N_6O_6S_1U_2$, trigonal, space group R-3c, a = 17.249(2), b = 17.249(2), c = 81.99(2) Å, V = 21127(6) $Å^3$, Z = 6, ρ_{calcd} = 1.168 Mg/m^3, $F(000)$ = 7704, $R_1(F)$ = 0.0563, $wR_2(F^2)$ = 0.1192 [$I > 2\sigma(I)$].

Crystallographic Details for 4

Orange plates, grown from diffusion of acetonitrile into a benzene solution of **4** at room temperature, were coated with isobutylene oil on a microscope slide. A crystal of approximate dimensions 0.23 × 0.18 × 0.10 mm^3 was selected and mounted on a nylon loop. A total of 57269 reflections ($-19 \leq h \leq 19$, $-19 \leq k \leq 19$, $-23 \leq l \leq 23$) were collected at T = 100(2) K in the θ range from 3.28 to 27.48º, of which 14944 were unique (R_{int} = 0.0485) and 13095 were observed [$I > 2\sigma(I)$] on a Bruker-Nonius KappaCCD diffractometer using Mo$K\alpha$ radiation (λ = 0.71073 Å, graphite monochromator). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12, Bruker AXS, Inc., 2002). The crystal under study was composed of a mixture of 98% of the selenido complex and 2% of the corresponding sulfido complex. Similar ratios were found in different crystals of this compound tested. The dinuclear complex is situated on a crystallographic inversion centre (on the bridging Se atom). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. The compound crystallizes with a total of four molecules of acetonitrile and four molecules of benzene. Two of the acetonitrile and two of the benzene solvate molecules are disordered over two different sites being occupied by approximately 50 % each. SIMU, ISOR and SAME restraints were applied in the refinement of the disorder. The residual peak and hole electron density were 2.230 and –2.439 e.Å^{-3}. The absorption coefficient was 2.798 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.0495, wR_2 = 0.0969, and GOF = 1.101 (all data). $C_{134}H_{192}N_{10}O_6S_{0.02}Se_{0,98}U_2$, triclinic, space group P-1, a = 14.861(2), b = 15.046(2), c = 17.804(2) Å, α = 70.93(1), β = 81.73(2), γ = 60.48(1)°, V = 3273.3(8) Å^3, Z = 1, ρ_{calcd} = 1.315 Mg/m^3, $F(000)$ = 1332, $R_1(F)$ = 0.0387, $wR_2(F^2)$ = 0.0920 [$I > 2\sigma(I)$].

Crystallographic Details for 7

Yellow block-shaped crystals, grown from a saturated solution of **7** in DME at room temperature, were coated with isobutylene oil on a microscope slide. A crystal of approximate dimensions 0.32 × 0.30 × 0.21 mm^3 was selected and mounted on a nylon loop. A total of 133321 reflections ($-28 \leq h \leq 28$, $-30 \leq k \leq 29$, $-31 \leq l \leq 31$) were collected at T = 150(2) K in the θ range from 3.19 to 26.37°, of which 25276 were unique (R_{int} = 0.0591) and 17140 were observed [$I > 2\sigma(I)$] on a Bruker-Nonius KappaCCD diffractometer using Mo$K\alpha$ radiation (λ = 0.71073 Å, graphite monochromator). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12, Bruker AXS, Inc., 2002). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron density were 6.944 and –3.187 e.Å^{-3}. The most significant residual electron density maxima were located in a distance of less than 1 Å from the two uranium centres and might be attributed to truncation effects. A PLATON analysis revealed the presence of two solvent accessible voids. Attempts to treat this with the SQUEEZE procedure did not lead to meaningful results. The compound crystallizes with a total of 3.5 molecules of DME per formula unit with one DME being occupied by approximately 50 % only indicating loss of included solvent. ISOR, SIMU and SAME restraints were applied in the refinement of the solvent molecules. The absorption coefficient was 2.674 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.1050, wR_2 = 0.1535, and GOF = 1.068 (all data). $C_{130}H_{187}N_2O_{17}S_1U_2$, monoclinic, space group $P2_1/c$, a = 22.837(2), b = 24.081(2), c = 25.250(2) Å, β = 116.123(8)°, V = 12468 (2) $Å^3$, Z = 4, ρ_{calcd} = 1.363 Mg/m^3, $F(000)$ = 5268, $R_1(F)$ = 0.0569, $wR_2(F^2)$ = 0.1242 [$I > 2\sigma(I)$].

Crystallographic Details for 8

Yellow-green prisms, grown from a saturated solution of **8** in DME at room temperature, were coated with isobutylene oil on a microscope slide. A crystal of approximate dimensions 0.44 × 0.27 × 0.22 mm^3 was selected and mounted on a nylon loop. A total of 132976 reflections ($-29 \leq h \leq 28$, $-30 \leq k \leq 28$, $-32 \leq l \leq 32$) were collected at T = 150(2) K in the θ range from 3.32 to 27.10°, of which 26758 were unique (R_{int} = 0.0937) and 16003 were observed [$I > 2\sigma(I)$] on a Bruker-Nonius KappaCCD diffractometer using Mo$K\alpha$ radiation (λ = 0.71073 Å, graphite monochromator). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12, Bruker AXS, Inc., 2002). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. This compound is isostructural with the corresponding sulfur-bridged complex **7**. A PLATON analysis revealed the presence of two solvent accessible voids. Attempts to treat this with the SQUEEZE procedure did not lead to meaningful results. The compound crystallizes with a total of 3.5 molecules of DME per formula unit with one DME being occupied by approximately 50 % only indicating loss of included solvent. ISOR, SIMU and SAME restraints were applied in the refinement of the solvent molecules. The residual peak and hole electron density were 2.199 and –1.080 e.$Å^{-3}$. The absorption coefficient was 2.942 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.1217, wR_2 = 0.1322, and GOF = 1.025 (all data). $C_{130}H_{187}N_2O_{17}Se_1U_2$, monoclinic, space group $P2_1/c$, a = 22.793(2), b = 24.1118(9), c = 25.319(3) Å, β = 116.09(1)°, V = 12497(2) $Å^3$, Z = 4, ρ_{calcd} = 1.384 Mg/m^3, $F(000)$ = 5340, $R_1(F)$ = 0.0520, $wR_2(F^2)$ = 0.1060 [$I > 2\sigma(I)$].

Crystallographic Details for 9

Yellow-orange prisms, grown from diffusion of DME into a THF solution of **9** at room temperature, were coated with isobutylene oil on a microscope slide. A crystal of approximate dimensions 0.26 × 0.23 × 0.19 mm^3 was selected and mounted on a nylon loop. A total of 124655 reflections ($-34 \leq h \leq 34$, $-20 \leq k \leq 20$, $-67 \leq l \leq 66$) were collected at $T = 150(2)$ K in the θ range from 3.34 to 25.68º, of which 23618 were unique ($R_{\text{int}} = 0.1075$) and 18973 were observed [$I > 2\sigma(I)$] on a Bruker-Nonius KappaCCD diffractometer using Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å, graphite monochromator). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12, Bruker AXS, Inc., 2002). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. Disorder is observed for one of the ligand arms, where two alternative orientations could be refined being occupied by 75(2) % for the major fraction and by 25(2) % for the minor fraction. The three DME molecules coordinating Na1 are also subjected to disorder. Two alternative positions of 50(2) % occupancy were refined. SIMU, ISOR and SAME restraints were applied in the refinement of the disordered structure parts. The residual peak and hole electron density were 1.934 and –1.969 e.Å^{-3}. The absorption coefficient was 2.566 mm^{-1}. The least-squares refinement converged normally with residuals of $R_1 = 0.1004$, w$R_2 = 0.2182$, and GOF = 1.481 (all data). $C_{132}H_{192}N_2Na_2O_{18}S_2U_2$, monoclinic, space group $C2/c$, $a = 28.397(3)$, $b = 17.161(2)$, $c = 55.426(11)$ Å, $\beta = 103.78(2)°$, $V = 26233(7)$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 1.358$ Mg/m^3, $F(000) = 11040$, $R_1(F) = 0.0805$, $wR_2(F^2) = 0.2101$ [$I > 2\sigma(I)$].

Crystallographic Details for 10

Orange block-shaped crystals, grown from diffusion of DME into a THF solution of **10** at room temperature, were coated with isobutylene oil on a microscope slide. A crystal of approximate dimensions 0.37 × 0.22 × 0.16 mm^3 was selected and mounted on a nylon loop. A total of 78022 reflections ($-31 \leq h \leq 31$, $-27 \leq k \leq 27$, $-34 \leq l \leq 23$) were collected at $T = 150(2)$ K in the θ range from 3.35 to 27.10º, of which 14761 were unique ($R_{\text{int}} = 0.0852$) and 10524 were observed [$I > 2\sigma(I)$] on a Bruker-Nonius KappaCCD diffractometer using Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å, graphite monochromator). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12, Bruker AXS, Inc., 2002). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. The dinuclear complex is situated on a crystallographic two-fold axis running through the center of the U1···U1B connecting line. A PLATON analysis revealed the presence of solvent accessible voids. Attempts to treat this with the SQUEEZE procedure did not lead to meaningful results. The crystal structure contains a major fraction of 95.3(2) % of the U bis-μ-selenide complex with a disorder of the Se site (two alternative positions were refined being occupied by 90.1(8) and 5.2(8) %). The minor fraction (atoms U1A and Se1A) of 4.7(2) % very likely represents a bis-μ-selenide complex. SIMU restraints were applied in the refinement of the disordered structure parts. The residual peak and hole electron density were 1.501 and –1.204 e.Å^{-3}. The absorption coefficient was 3.022 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.0897, wR_2 = 0.1345, and GOF = 1.082 (all data). $C_{132}H_{192}N_2Na_2O_{18}Se_2U_2$, monoclinic, space group $C2/c$, a = 24.887(5), b = 21.404(4), c = 26.847(5) Å, β = 110.322(9)°, V = 13411(4) Å^3, Z = 4, ρ_{calcd} = 1.374 Mg/m^3, $F(000)$ = 5664, $R_1(F)$ = 0.0527, $wR_2(F^2)$ = 0.1219 [$I > 2\sigma(I)$].

Crystallographic Details for 11

Orange plates, grown from diffusion of DME into a THF solution of **11** at room temperature, were coated with isobutylene oil on a microscope slide. A crystal of approximate dimensions 0.27 × 0.15 × 0.06 mm^3 was selected and mounted on a nylon loop. A total of 82862 reflections ($-31 \leq h \leq 30$, $-27 \leq k \leq 27$, $-34 \leq l \leq 34$) were collected at T = 150(2) K in the θ range from 3.35 to 27.10°, of which 14851 were unique (R_{int} = 0.0898) and 10948 were observed [$I > 2\sigma(I)$] on a Bruker-Nonius KappaCCD diffractometer using Mo$K\alpha$ radiation (λ = 0.71073 Å, graphite monochromator). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12, Bruker AXS, Inc., 2002). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. All three DME molecules coordinating the Na counterion are disordered. Two alternative sites were refined giving site occupancies of 70.6(5) % for the main fraction and 29.4(5) % for the minor fraction (denoted by the addendum A). The compound crystallizes with one THF per formula unit that is disordered on a crystallographic twofold axis (Wyckoff position 4e) and only partially occupied (25%).

This compound is isostructural with the corresponding bis-μ-selenide complex **10**. The residual peak and hole electron density were 2.019 and –1.098 e.Å^{-3}. The absorption coefficient was 2.889 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.0794, wR_2 = 0.1104, and GOF = 1.068 (all data). $C_{134}H_{196}N_2Na_2O_{18.5}Te_2U_2$, monoclinic, space group *C*2/c, *a* = 24.818(2), *b* = 21.454(2), *c* = 27.070(3) Å, β = 110.585(11)°, *V* = 13493(2) Å^3, *Z* = 4, ρ_{calcd} = 1.432 Mg/m^3, *F*(000) = 5888, $R_1(F)$ = 0.0477, $wR_2(F^2)$ = 0.1003 [$I > 2\sigma(I)$].

Crystallographic Details for 12

Orange-brown prisms, grown from a saturated solution of **12** in DME at room temperature, were coated with isobutylene oil on a microscope slide. A crystal of approximate dimensions 0.23 × 0.18 × 0.16 mm^3 was selected and mounted on a nylon loop. A total of 78618 reflections ($-19 \leq h \leq 19$, $-21 \leq k \leq 21$, $-28 \leq l \leq 27$) were collected at *T* = 150(2) K in the θ range from 3.14 to 27.10°, of which 23840 were unique (R_{int} = 0.1035) and 15343 were observed [$I > 2\sigma(I)$] on a Bruker-Nonius KappaCCD diffractometer using Mo*K*α radiation (λ = 0.71073 Å, graphite monochromator). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12, Bruker AXS, Inc., 2002). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. One of the ligand arms around U2 is disordered. Two alternative orientations of 50.1(4) and 49.9(4) % occupancy for the atoms O6, C70 – C75, C98 – C108 and O106, C170 – C175, C198 – C208, respectively, were refined. The compound crystallizes with a total of 2.5 molecules of DME with the 0.5 DME molecule being situated at the site of the disordered ligand arm. ISOR, SIMU and SAME restraints were applied in the refinement of the disordered structure parts. The residual peak and hole electron density were 4.288 and –2.099 e.Å^{-3}. The absorption coefficient was 3.053 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.1064, wR_2 = 0.1188, and GOF = 1.017 (all data). $C_{123}H_{162}N_3O_{14}U_2$, triclinic, space group *P*-1, *a* = 15.172(2), *b* = 16.926(2), *c* = 21.898(2) Å, α = 99.027(6)°, β = 100.160(7)°, , γ = 96.211(8)°, *V* = 5413.0(8) Å^3, *Z* = 24, ρ_{calcd} = 1.462 Mg/m^3, *F*(000) = 2434, $R_1(F)$ = 0.0522, $wR_2(F^2)$ = 0.1000 [$I > 2\sigma(I)$].

Additional Temperature-Dependent Magnetization Data

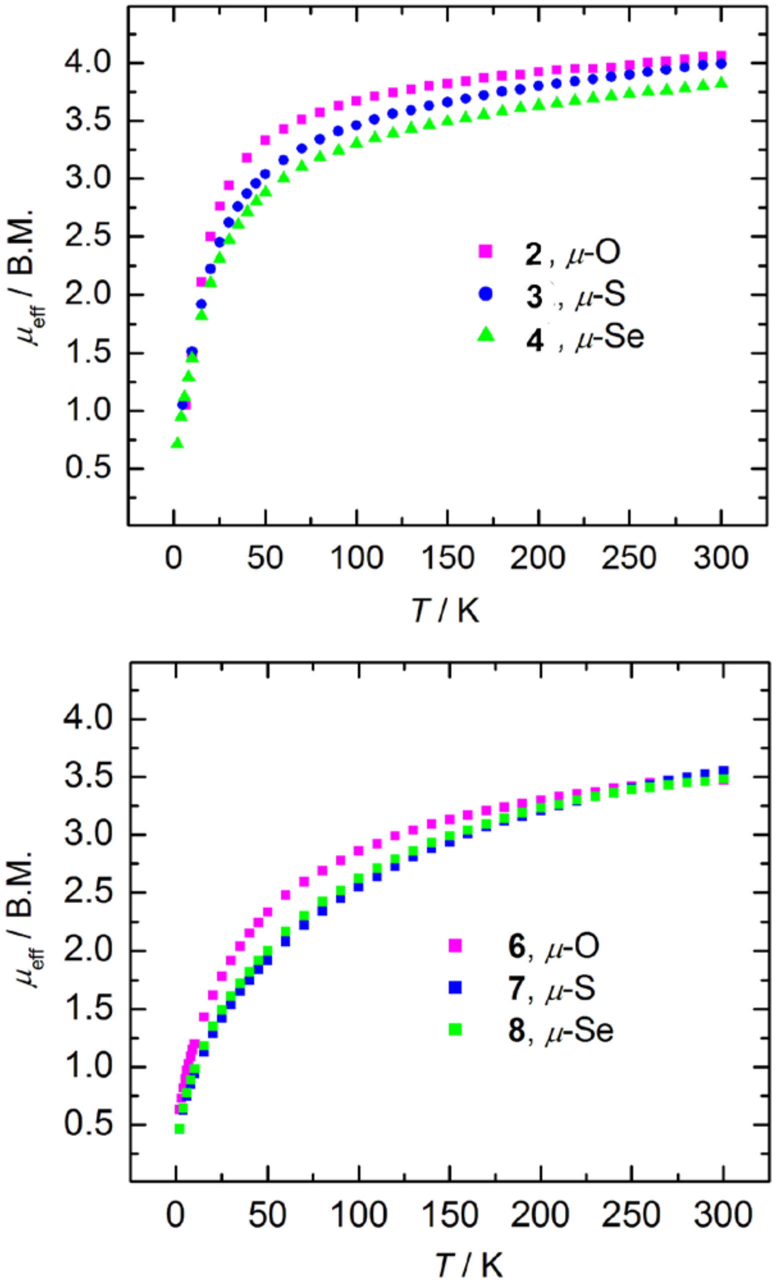

Figure S1. Variable temperature magnetization data for complexes of type [{(($^{t\text{-}Bu}$ArO)$_3$tacn)U}$_2$(μ-E)], E = O (**2**), S (**3**), Se (**4**) (top) and [{((^{Ad}ArO)$_3$N)U}$_2$(μ-E)], E = O (**6**), S (**7**), Se (**8**) (bottom).

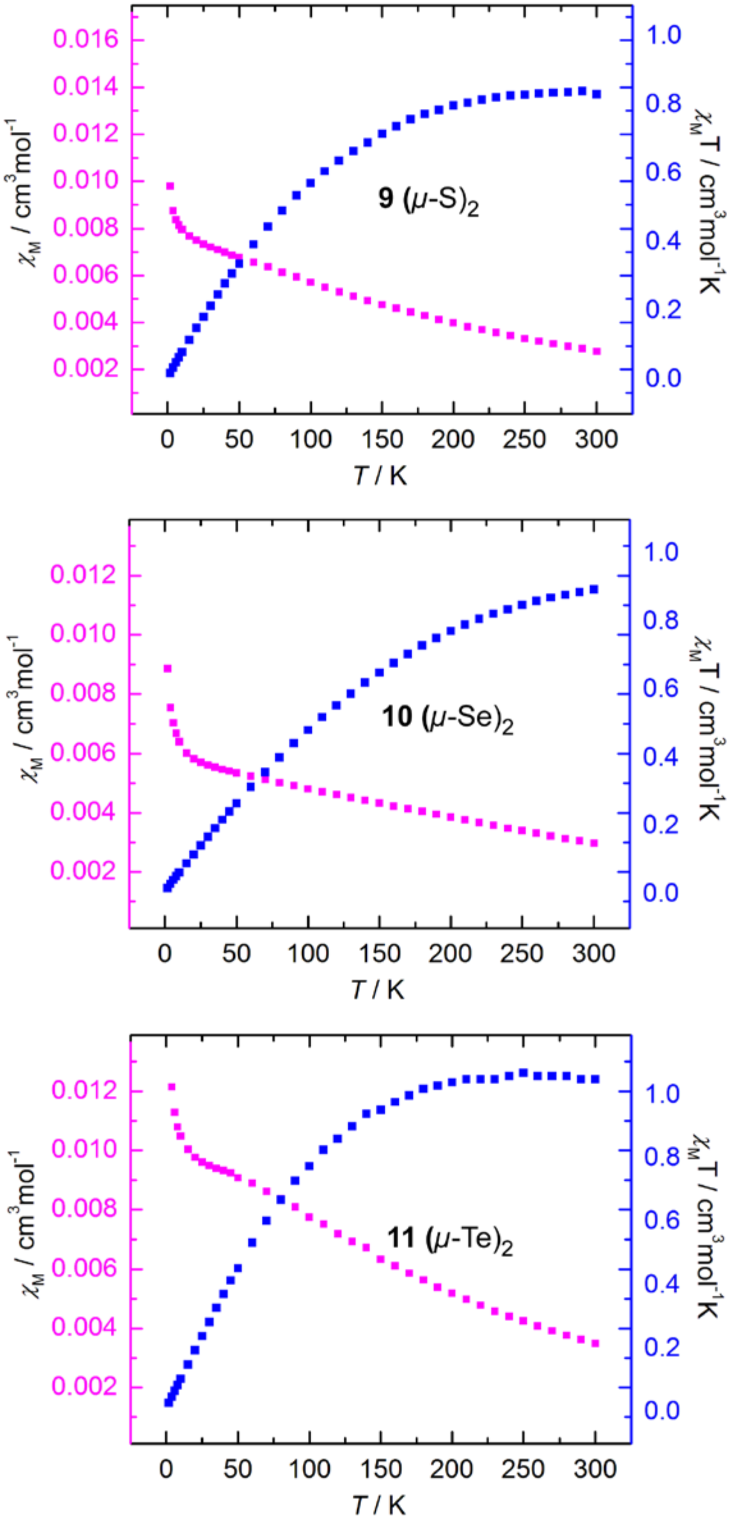

Figure S2. Magnetic susceptibility plots for U(IV) species [{((^{Ad}ArO)$_3$N)U}$_2$(μ-E)$_2$] (E = S (**9**, top); Se (**10**, middle); Te (**11**, bottom) plotted as a function of χ_M *vs.* T in magenta and χ_MT *vs.* T in blue. Data were corrected for underlying diamagnetism.

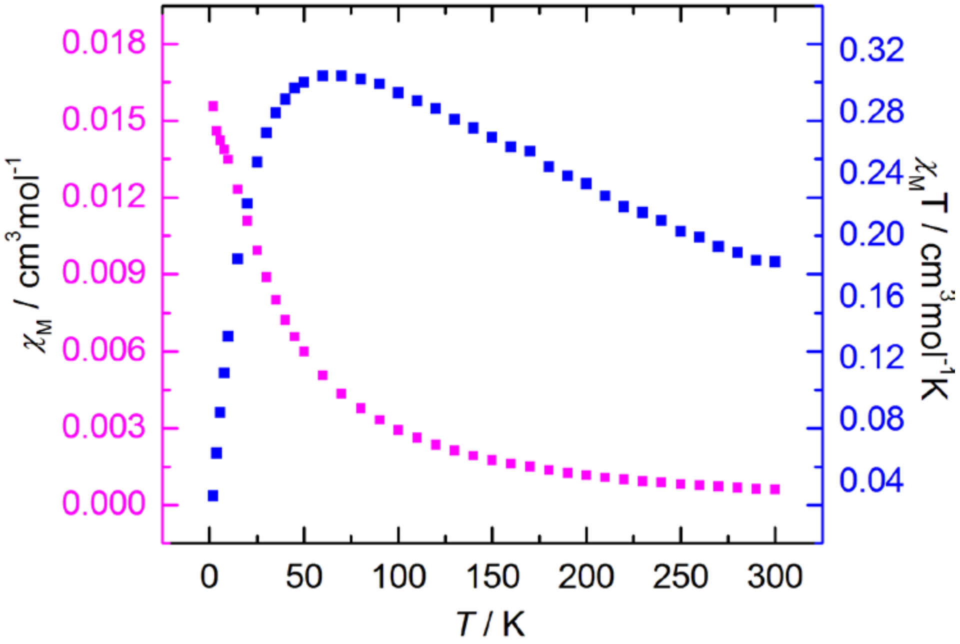

Figure S3. Magnetic susceptibility plots for U(V) species $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}O)_2]$ (**12**) plotted as a function of χ_M vs. T in magenta and χ_MT *vs.* T in blue. Data were corrected for underlying diamagnetism.