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The Synthesis and Characterization of Four New Uranium(IV) Chlorophosphates: $UCl_4(POCl_3)$, $[U_2Cl_9][PCl_4]$, $UCl_3(PO_2Cl_2)$, and $U_2Cl_8(POCl_3)$

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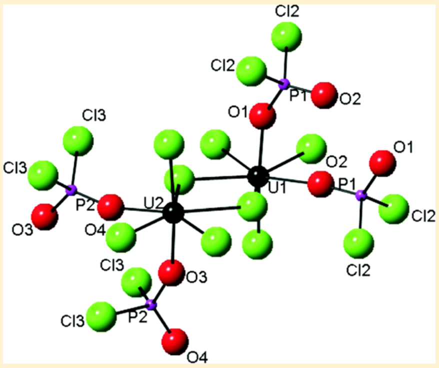
Supporting Information

ABSTRACT: The new uranium(IV) chlorophosphate compounds $UCl_4(POCl_3)$ and $[U_2Cl_9][PCl_4]$ have been synthesized by the solid-state reactions of U, P_2O_5, and PCl_5 at 648 K; the compounds $UCl_3(PO_2Cl_2)$ and $U_2Cl_8(POCl_3)$ have been synthesized at 648 K with the same reactants plus added S. Their structures are, respectively, chainlike, a simple salt, three-dimensional, and sheetlike. From ab initio calculations, $U_2Cl_8(POCl_3)$ and $UCl_3(PO_2Cl_2)$ are found to be ferromagnetic, whereas $UCl_4(POCl_3)$ is found to be antiferromagnetic. $U_2Cl_8(POCl_3)$ is a strong metal, whereas $UCl_3(PO_2Cl_2)$ is a weaker metal. In contrast, $UCl_4(POCl_3)$ has a finite band gap, with a value of 0.35 eV.



INTRODUCTION

The discovery and characterization of uranium oxides has been the subject of prolonged research.[1,2] Their chemistry is dominated by U(VI) in the form of the very stable uranyl ion, UO_2^{2+}. There are far fewer solid-state uranium oxides that contain U(IV). These include a series of uranium phosphates,[3−5] molybdates,[6,7] niobates,[8−10] tantalates,[11,12] tungstates,[13] $UTa_2O(S_2)_3Cl_6$,[14] TlU_3OF_{11},[15] $UOCl_2$,[16] $U_2O_2Cl_5$,[17] $Ba_7UM_2S_{12.5}O_{0.5}$ (M = V, Fe),[18] UOQ (Q = S, Se, Te),[19] and $UF_3(H_2O)(C_2O_4)_{0.5}$.[20]

Most of the known uranium(IV) oxides are uranium phosphates.[4,5,21,22] The coordination environment of the U atoms in these is often either eight-coordinate dodecahedral, as in $U_2(PO_4)(P_3O_{10})$,[23] or seven-coordinate pentagonal-bipyramidal, as in $U_2O(PO_4)_2$[21] and the mixed U(IV)/U(VI) compound $U(UO_2)_2(PO_4)_2$.[24] It is typical in these coordination environments for each O atom to be shared between U and P, thus leaving no terminal O atoms. This differs from uranyl chemistry, in which the axial O atoms are typically only bonded to U. Most of these uranium(IV) compounds are oxygen-rich and contain only oxygen as the primary coordination anion, whether in the form of O^{2-}, OH^-, or H_2O.

Although uranium(IV) compounds that contain both oxygen and halide anions are known and include TlU_3OF_{11},[15] $UOCl_2$,[16] $U_2O_2Cl_5$,[17] and $UF_3(H_2O)(C_2O_4)_{0.5}$[20] the only uranium(IV) phosphate compounds to include halide anions are $UXPO_4 \cdot nH_2O$ (X = F, Cl, Br).[25,26] In part, the reason for this is the stability of the known phases $U(UO_2)_2(PO_4)_2$,[24] $U_2(PO_4)(P_3O_{10})$,[23] $U_2O(PO_4)_2$,[21] and α-$U(P_2O_7)$.[22] (Some of these compounds, incidentally, were previously misidentified in diverse compositions.)[3]

Here, we present the synthesis and characterization of the new uranium(IV) compounds $UCl_4(POCl_3)$, $[U_2Cl_9][PCl_4]$, $UCl_3(PO_2Cl_2)$, and $U_2Cl_8(POCl_3)$ as well as the electronic structure properties from ab initio calculations on the three O-containing compounds.

EXPERIMENTAL METHODS

Syntheses. The following reactants were used as received: P_2O_5 (Mallickrodt 99.5%), PCl_5 (Alfa 99.998%), and S (Mallinckrodt 99.6%). U powder was obtained through the hydridization of depleted U turnings (IBI Laboratories), followed by decomposition of the hydride under vacuum.[27] The reactants were loaded into carbon-coated fused-silica tubes in an Ar-filled glovebox, evacuated to 10^{-4} Torr, and then flame-sealed.

Semiquantitative EDX analysis of the products of the reactions were obtained with the use of a Hitachi S-3400 SEM microscope.

Each tube was placed in a computer-controlled furnace and heated to 648 K over 24 h and held there for 96 h. The reaction was then cooled to 373 at 2 K h^{-1}, and then to 298 K in 24 h. As soon as a reaction tube was opened, the reaction products were placed under paratone oil to prevent decomposition. A few crystals were then manually isolated, and one was chosen for characterization by single-crystal X-ray diffraction methods. The crystals decompose rapidly upon exposure to air, and all of the products decompose within a day, even those placed under oil.

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Table 1. Crystallographic Data for $UCl_4(POCl_3)$, $[U_2Cl_9][PCl_4]$, $UCl_3(PO_2Cl_2)$, and $U_2Cl_8(POCl_3)$

	$UCl_4(POCl_3)$	$[U_2Cl_9][PCl_4]$	$UCl_3(PO_2Cl_2)$	$U_2Cl_8(POCl_3)$
crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	C_{2h}^5-$P2_1/c$	D_{2h}^{10}-$Pccn$	D_{2h}^{9}-$Pbam$	D_{2h}^{16}-$Pnma$
a/Å	8.9155 (2)	8.3695 (2)	9.0298 (4)	8.4402 (2)
b/Å	8.4329 (2)	13.4190 (3)	24.1890 (12)	8.3987 (2)
c/Å	17.1934 (4)	16.9609 (4)	8.5013 (3)	23.0134 (6)
V/Å^3	1113.56 (5)	1904.88 (8)	1856.87 (14)	1631.34 (7)
β/deg	120.5202 (12)	90	90	90
T/K	100(2)	100(2)	100(2)	100(2)
Z	4	4	8	4
$R(F)$ $[I > 2\sigma(I)]^a$	0.0297	0.0268	0.0489	0.0416
$R_w(F_o^2)^b$	0.0637	0.0542	0.1142	0.0846
q^c	0.0232	0.0115	0.0559	0.000

$^a R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. $^b R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$ for all data. $^c w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

Synthesis of $UCl_4(POCl_3)$. In an effort to synthesize a mixed-anion uranium phosphorus compound, an initial reaction was loaded with U (0.0300 g, 0.126 mmol), P_2O_5 (0.0072 g, 0.0252 mmol), and PCl_5 (0.0750 g, 0.3602 mmol). The reaction afforded green plates of $UCl_4(POCl_3)$ in about 75 wt % yield based on U, as well as a green powder of composition U/P/Cl and excess PCl_5.

Synthesis of $[U_2Cl_9][PCl_4]$. Concurrent to the reaction for $UCl_4(POCl_3)$, a second reaction was loaded with identical amounts of reactants and simultaneously heated in the same furnace under the same heating profile. Surprisingly, the reaction afforded a different product, namely, green needles of $[U_2Cl_9][PCl_4]$ in about 75 wt % yield based on U, along with a green powder of composition U/P/Cl and excess PCl_5.

Synthesis of $UCl_3(PO_2Cl_2)$. In an effort to synthesize a uranyl oxysulfide, a reaction was loaded with U (0.0300 g, 0.126 mmol), P_2O_5 (0.0072 g, 0.252 mmol), S (0.0363 g, 1.134 mmol), and PCl_5 (0.0750 g, 0.3602 mmol). The reaction afforded green plates of $UCl_3(PO_2Cl_2)$ as the major product in about 90 wt % yield based on uranium, as well as excess PCl_5 and powdered material of the composition U/P/S/Cl.

Synthesis of $U_2Cl_8(POCl_3)$. In an effort to reproduce the synthesis of $UCl_3(PO_2Cl_2)$, a series of reactions containing U, P_2O_5, S, and PCl_5 were loaded with varying stoichiometries. Each reaction yielded only $UCl_4(POCl_3)$ as a crystalline phase, except for one. In that one, the contents were U (0.0300 g, 0.126 mmol), P_2O_5 (0.0072 g, 0.0252 mmol), S (0.0121 g, 0.378 mmol), and PCl_5 (0.0750 g, 0.3602 mmol). The reaction afforded green plates of $UCl_4(POCl_3)$ in about 75 wt % yield based upon U along with a few yellow plates (less than 5 wt %) of $U_2Cl_8(POCl_3)$, powdered material of composition U/P/S/Cl, and excess PCl_5.

Structure Determinations. Single-crystal X-ray diffraction data were collected at 100 K on an APEX2 X-ray diffractometer equipped with graphite-monochromatized MoKα radiation.[28] The crystal-to-detector distance was 60 mm; the exposure time was 10 s/frame. Collection of intensity data, cell refinement, and data reduction were performed using APEX2 as a series of 0.3° scans in φ and ω.[28] Face-indexed absorption, incident beam, and decay corrections were performed by the program SADABS.[29] Precession images derived from the data showed no evidence of supercells or modulations. All structures were solved and refined in a straightforward manner with the use of the Shelx-13 suite of programs.[29,30] The PCl_4 group in $[U_2Cl_9][PCl_4]$ is disordered over two orientations in which the P1 and Cl1 atoms translate across a plane created by two Cl4 atoms and one Cl8 atom. As there is no evidence for a larger unit cell, the P1 and Cl1 sites have been refined as being half-occupied. Atom positions were standardized using the program STRUCTURE TIDY.[31] Crystallographic images were made using the program CRYSTALMAKER.[32] Further details are given in Table 1 and the Supporting Information.

Ab Initio Calculations. Ab initio calculations have been performed with the Vienna Ab initio Simulation Package.[33,34] In particular, the projector augmented wave method[35] was used, together with density functional theory.[36] In this framework, the Kohn–Sham equations[37] were solved using a combination of plane waves and localized orbitals as the basis set. The exchange-correlation potential was described at the generalized gradient approximation[38] level including spin polarization. In all calculations, the geometries used were the experimental ones. The ground-state magnetic order was identified by trying all possible magnetic orders within one crystallographic unit cell and retaining the one with the lowest total energy. The default cutoff for the wave function and a k-point mesh of 6 × 6 × 1 to sample the Brillouin zone were used to reach convergence.

■ RESULTS

Syntheses. Following our recent syntheses of the mixed-anion uranium oxychalcogenides $Na_2Ba_2UO_2S_4$[39] and $U_7O_2Se_{12}$,[40] we have explored different oxygen-transfer agents. Here, we chose P_2O_5 because of the possibility of incorporating P as well a O. PCl_5 was chosen as a flux in the reactions because of its low melting point (440 K). Several reactions, in addition to those described above, involved alkali-halide fluxes, but these produced only green plates of $UCl_4(POCl_3)$. Following the initial reactions with only P_2O_5 and PCl_5, additional reactions with S as well were loaded with the target being uranyl sulfides. Further reactions loaded with P_2S_5 in place of PCl_5 did not yield crystalline products.

The uranium(IV) compounds $UCl_4(POCl_3)$, $[U_2Cl_9][PCl_4]$, $UCl_3(PO_2Cl_2)$, and $U_2Cl_8(POCl_3)$ were synthesized from the reaction of U powder, P_2O_5, and PCl_5 at 648 K. In the reactions that produced $UCl_3(PO_2Cl_2)$ and $U_2Cl_8(POCl_3)$, S was also present, but was not found in the crystalline products. $UCl_3(PO_2Cl_2)$, $U_2Cl_8(POCl_3)$, and $[U_2Cl_9][PCl_4]$ were only found in one reaction, whereas multiple reactions led to $UCl_4(POCl_3)$. Although all phases are very unstable and decompose immediately upon exposure to air, $UCl_4(POCl_3)$ appears to be the thermodynamically stable phase. Attempts were made to obtain single-crystal Raman spectra, but the crystals decomposed as data were being collected. Instability prevented the collection and preservation of sufficient crystals for magnetic studies.

For all four compounds, their formulas may be charge-balanced by assigning oxidation states of +4, +5, −1, and −2 to U, P, Cl, and O, respectively. In these reactions, U^0 was oxidized to U^{4+}. For the first two syntheses, this must have been accomplished by P^{5+} being reduced; for the last two syntheses, either P^{5+} or S^0 could have been reduced.

Crystal Structure of $UCl_4(POCl_3)$. The compound $UCl_4(POCl_3)$ crystallizes with four formula units in the monoclinic space group C_{2h}^{5}-$P2_1/c$. The asymmetric unit consists of one U site, seven Cl sites, one P site, and one O site, all in general positions.

$UCl_4(POCl_3)$ has an infinite chainlike structure (Figure 1). Each U atom is coordinated by six Cl atoms and one O atom in a pentagonal-bipyramidal arrangement (Figure 2). The six Cl atoms occupy two of the axial positions and four of the equatorial positions. The O atom occupies the remaining equatorial position. The infinite chains are formed when each U atom edge-shares two of the equatorial Cl atoms with other U atoms in two directions (Figure 3). The equatorial O atom is corner-shared with a terminal PCl_3 unit that does not allow the chains to connect into a larger framework. Within the chain, the directions of the equatorial O atoms alternate. Each P atom within the structure is coordinated tetrahedrally by three Cl atoms and one O atom. The O atom is corner-shared with the U atom, and the three Cl atoms are terminal.

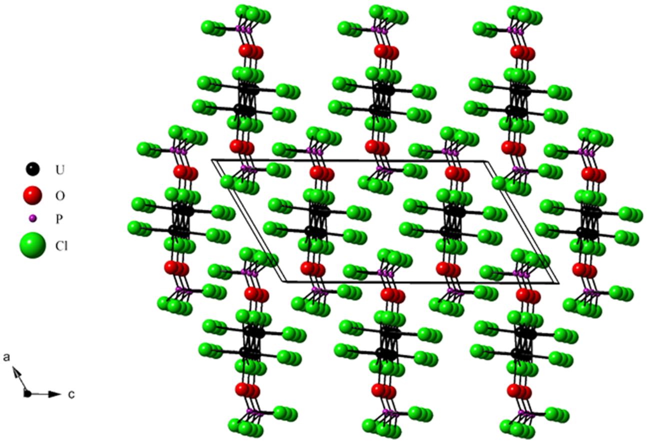

Figure 1. Structure of $UCl_4(POCl_3)$ viewed nearly down *b*.

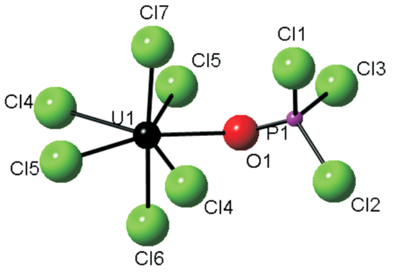

Figure 2. Coordination environments of U and P in the structure of $UCl_4(POCl_3)$.

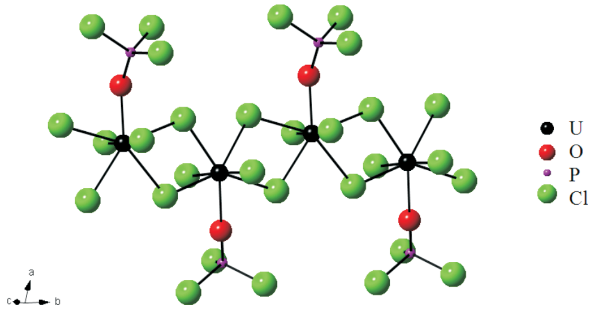

Figure 3. Infinite chains in the structure of $UCl_4(POCl_3)$.

Selected interatomic distances for $UCl_4(POCl_3)$ can be found in Table 2. The U–O distance of 2.360(2) Å may be compared with the distances of 2.18(2) and 2.23(2) Å in $UClPO_4{\cdot}2H_2O$.[26] The U–Cl_{ax} distances are 2.526(1) and 2.536(1) Å, and the Cl–U–Cl angle is 176.52 (3)°. The U–Cl_{eq} distances range from 2.769 (1) to 2.771(1) Å. These distances are consistent with those of 2.638(4)–2.869(3) Å in UCl_4[41] and 2.725(2)–2.742(2) Å in $U_2O_2Cl_5$.[17] The P–O distance of 1.475(3) Å is consistent with the P–O distances of 1.466(4)–1.487(3) Å in $[PO_2Cl_2]$ units[42] as well as those of 1.51(2)–1.53(2) Å in $UClPO_4{\cdot}2H_2O$.[26] The P–Cl distances of 1.952(1), 1.955(1), and 1.960(1) Å, are slightly longer than that of 1.929(2) Å in $[PCl_4][SbF_6]$.[43]

Table 2. Selected Interatomic Distances[a] for $UCl_4(POCl_3)$ and $[U_2Cl_9][PCl_4]$[b]

$UCl_4(POCl_3)$	distance (Å)	$[U_2Cl_9][PCl_4]$	distance (Å)
U1–O1	2.360 (2)	U1–Cl6	2.526 (1)
U1–Cl7	2.526 (1)	U1–Cl5	2.536 (1)
U1–Cl6	2.536 (1)	U1–Cl2	2.751 (1)
U1–Cl4	2.769 (1)	U1–Cl3	2.754 (1)
U1–Cl4	2.770 (1)	U1–Cl7	2.759 (1)
U1–Cl5	2.771 (1)	U1–Cl2	2.762 (1)
U1–Cl5	2.771 (1)	U1–Cl3	2.780 (1)
P1–O1	1.475 (3)	P1–Cl8	1.874 (3)
P1–Cl2	1.952 (1)	P1–Cl4	1.880 (3)
P1–Cl1	1.955 (1)	P1–Cl4	1.892 (3)
P1–Cl3	1.960 (1)	P1–Cl1	1.934 (3)

[a]All interatomic distances have been rounded to three significant figures. [b]All U–U interatomic distances are longer than 4.4 Å.

Crystal Structure of $[U_2Cl_9][PCl_4]$. The structure of $[U_2Cl_9][PCl_4]$ crystallizes with four formula units in the orthorhombic space group D_{2h}^{10}-*Pccn*. The structure is composed of one U site, eight Cl sites, and one P site. All are on general positions except, for atoms Cl7 and Cl8, which have site symmetry ..2.

$[U_2Cl_9][PCl_4]$ is a salt. Its structure is made up of infinite $[U_2Cl_9]$ sheets separated by $[PCl_4]$ units (Figure 4). As in $UCl_4(POCl_3)$ and $UCl_3(PO_2Cl_2)$, each U atom in $[U_2Cl_9]$-

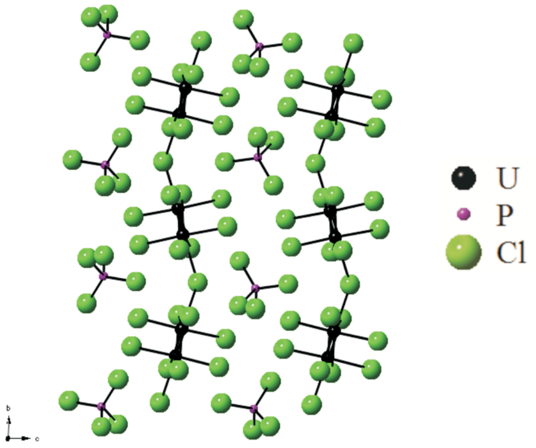

Figure 4. Packing of the infinite sheets in the structure of $[U_2Cl_9][PCl_4]$. The disorder of the $[PCl_4]$ unit is not shown.

[PCl_4] is seven-coordinate in a pentagonal-bipyramidal arrangement. Similar to $UCl_4(POCl_3)$ and $UCl_3(PO_2Cl_2)$, each U atom edge-shares two equatorial Cl atoms with other U atoms in two directions. The infinite sheets are formed when U atoms from different chains corner-share their remaining equatorial Cl atoms (Figure 5). The space between these sheets is occupied by tetrahedral [PCl_4] units. These [PCl_4] units can rotate within the channels to crystallize in two orientations.

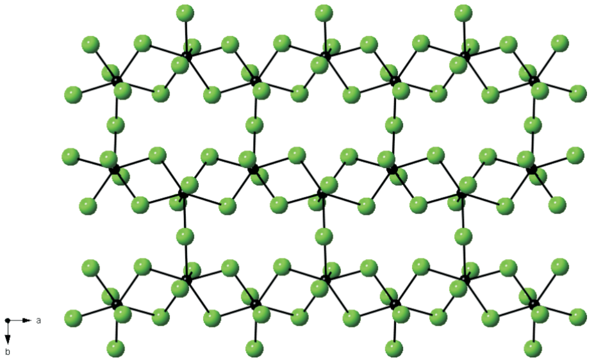

Figure 5. Infinite sheets of [U_2Cl_9] in the structure of [U_2Cl_9][PCl_4].

Interatomic distances for [U_2Cl_9][PCl_4] can be found in Table 2. The U−Cl_{ax} distances are 2.526(1) and 2.536(1) Å; the Cl−U−Cl angle is 177.71(4)°. The U−Cl_{eq} distances range from 2.751(1) to 2.780(1) Å and are consistent with distances of 2.638(4)−2.869(3) Å in UCl_4[41] and 2.725(2)−2.742(2) Å in $U_2O_2Cl_5$.[17] The U−Cl_{ax} distances are significantly shorter, as expected because these axial Cl atoms are not shared between U atoms.

Crystal Structure of $UCl_3(PO_2Cl_2)$. $UCl_3(PO_2Cl_2)$ crystallizes with eight formula units in the orthorhombic space group D_{2h}^{9}-*Pbam*. The asymmetric unit consists of two U sites, six Cl sites, two P sites, and four O sites. All sites have site symmetry *.m.*, except for atoms Cl1, Cl2, Cl3, and Cl4, which are in general positions.

The structure of $UCl_3(PO_2Cl_2)$ is three-dimensional and consists of infinite U/Cl chains linked together by [PO_2Cl_2] units (Figure 6). The U atoms in $UCl_3(PO_2Cl_2)$ are seven-coordinate with two O atoms and five Cl atoms in a pentagonal-bipyramidal arrangement (Figure 7). In this U^{4+} structure, the O atoms within the bipyramid occupy one of the axial positions and one of the equatorial positions. This differs from the commonly observed U^{6+} uranyl ion (UO_2^{2+}), in which O atoms occupy both of the axial positions. The Cl atoms occupy the second axial position and the four remaining equatorial positions. Within the infinite U chains, each U atom edge-shares two equatorial Cl atoms in each direction with the other U atoms in the chain (Figure 8). Each U atom then corner-shares each of its O atoms with P atoms.

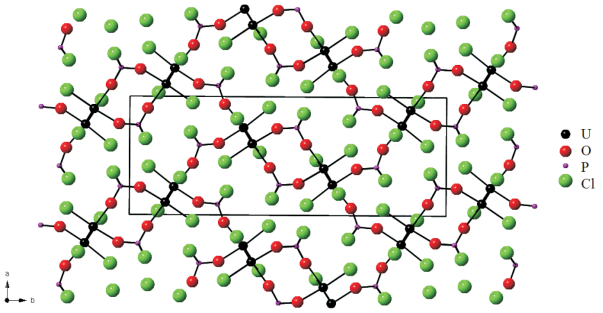

Figure 6. Framework structure of $UCl_3(PO_2Cl_2)$ viewed down the *c* axis.

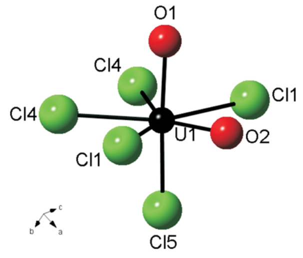

Figure 7. Coordination environment of U in the structure of $UCl_3(PO_2Cl_2)$.

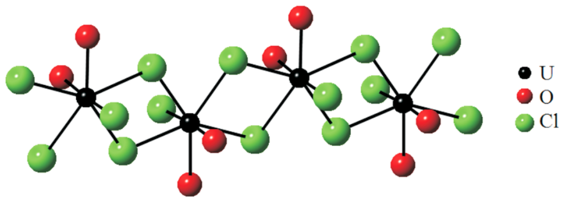

Figure 8. Infinite chains in the structure of $UCl_3(PO_2Cl_2)$.

The U−O distances (Table 3), which range from 2.219(7) to 2.299(7) Å, may be compared with those of 2.078−2.514 Å in $U_2O(PO_4)_2$, in which the U atom is coordinated to seven O atoms in a pentagonal bipyramid.[21] The axial U1−Cl distance is 2.508(2) Å, and the axial U2−Cl distance is 2.482(3) Å. The equatorial U−Cl distances range from 2.747(2) to 2.771(2) Å, which are again consistent with distances in UCl_4[41] and $U_2O_2Cl_5$.[17] Note that the axial U−Cl distances are significantly shorter than the equatorial distances. This likely occurs because the axial Cl atoms are not shared with other U atoms as are the equatorial Cl atoms. The O_{ax}−U−Cl_{ax} angle in this U^{4+} structure is 176.3(2)°, essentially the same as that in U^{6+}

Table 3. Selected Interatomic Distances[a] for $UCl_3(PO_2Cl_2)$ and $U_2Cl_8(POCl_3)$[b]

$UCl_3(PO_2Cl_2)$	distance (Å)	$U_2Cl_8(POCl_3)$	distance (Å)
U1−O1	2.238 (6)	U1−O1	2.366 (7)
U1−O2	2.281 (6)	U1−Cl5	2.510 (2)
U1−Cl5	2.508 (2)	U1−Cl7	2.524 (2)
U1−Cl4 × 2	2.747 (2)	U1−Cl3 × 2	2.748 (1)
U1−Cl1 × 2	2.771 (2)	U1−Cl2 × 2	2.792 (1)
U2−O3	2.219 (7)	U2−Cl2 × 2	2.682 (1)
U2−O4	2.299 (7)	U2−Cl6	2.682 (2)
U2−Cl6	2.482 (3)	U2−Cl8	2.685 (2)
U2−Cl1 × 2	2.752 (2)	U2−Cl3 × 2	2.786 (1)
U2−Cl4 × 2	2.764 (2)	U2−Cl6	2.833 (2)
P1−O2	1.488 (6)	U2−Cl8	2.897 (2)
P1−O1	1.498 (7)	P1−O1	1.460 (7)
P1−Cl2 × 2	1.964 (3)	P1−Cl1 × 2	1.954 (2)
P2−O4	1.489 (7)	P1−Cl4	1.967 (4)
P2−O3	1.500 (7)		
P2−Cl3 × 2	1.969 (3)		

[a] All interatomic distances have been rounded to three significant figures. [b] All U−U interatomic distances are longer than 4.4 Å.

structures containing the UO_2^{2+} ions with pentagonal-bipyramidal coordination environments.[44]

Each P atom within the structure is coordinated by two Cl atoms and two O atoms in a tetrahedral environment giving $[PO_2Cl_2]$ units (Figure 9). These tetrahedra connect the infinite U chains into the three-dimensional framework by corner-sharing each of the O atoms with a different chain. The Cl atoms within the $[PO_2Cl_2]$ units are not shared. The P–O distances range from 1.488(6) to 1.500(7) Å, and the P–Cl distances are1.964(3) and 1.969(3) Å. These distances are typical for $[PO_2Cl_2]$ units.[42]

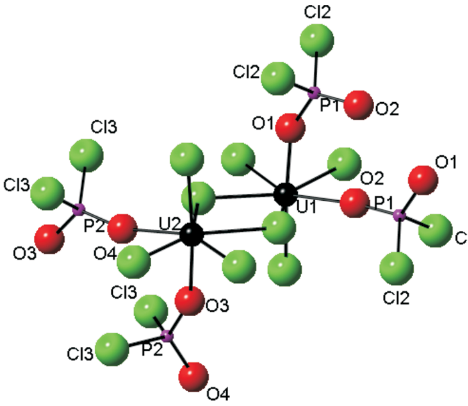

Figure 9. Coordination environment of P and U in the structure of $UCl_3(PO_2Cl_2)$.

Crystal Structure of $U_2Cl_8(POCl_3)$. $U_2Cl_8(POCl_3)$ crystallizes with four formula units in the orthorhombic space group D_{2h}^{16}-*Pnma*. The structure is composed of two U sites, eight Cl sites, one P site, and one O site. All sites have symmetry *..m*, except for atoms Cl1, Cl2, and Cl3, which are in general positions.

The structure of $U_2Cl_8(POCl_3)$ is made up of close-packed infinite sheets (Figure 10). There are two types of U atoms in the structure. Atom U1 is coordinated by one O atom and six Cl atoms in a pentagonal-bipyramidal arrangement, and atom U2 is coordinated by eight Cl atoms in a dodecahedron (Figure 11). Each U1 atom edge-shares two Cl_{eq} atoms, each attached to two U2 atoms to form infinite chains along the *b* axis (Figure 12). These infinite chains then grow into infinite sheets when the U2 atoms edge-share the remaining Cl atoms with other U2 atoms from other infinite chains to give sheets perpendicular to *c*. Each U1 atom edge-shares its one O atom with atom P1 to create a terminal $[POCl_3]$ unit. These terminal $[POCl_3]$ units appear both above and below the infinite sheets along the *c* axis. The packing of the infinite sheets causes these $[POCl_3]$ units to pack between the $[POCl_3]$ units from the sheets above and below.

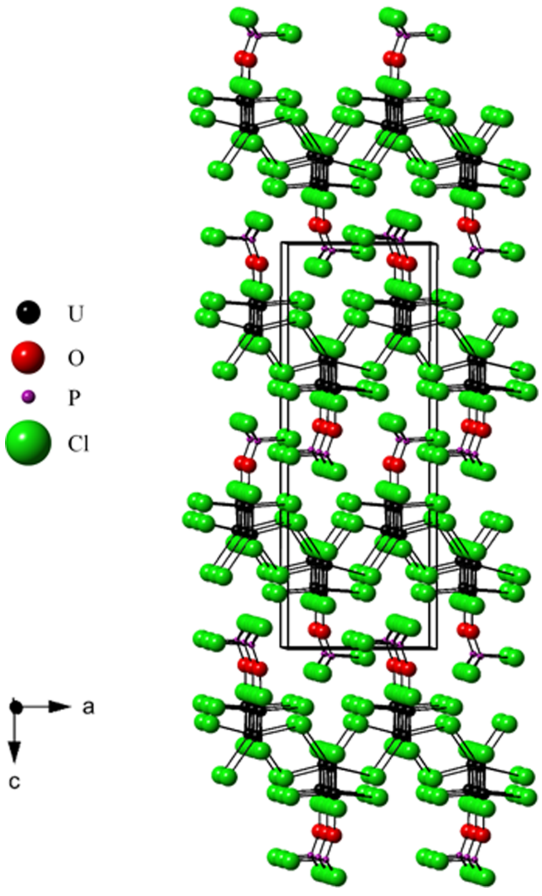

Figure 10. Closely packed sheets in the structure of $U_2Cl_8(POCl_3)$.

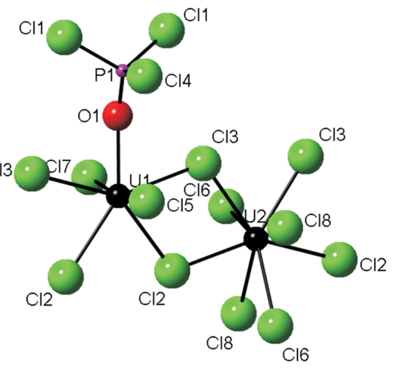

Figure 11. Coordination of atoms U1 and U2 in the structure of $U_2Cl_8(POCl_3)$.

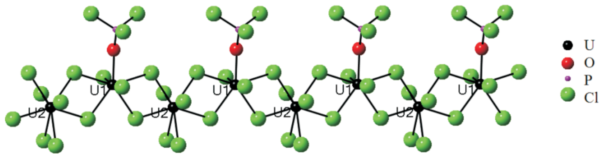

Figure 12. Infinite chains in the structure of $U_2Cl_8(POCl_3)$.

Selected interatomic distances for $U_2Cl_8(POCl_3)$ can be found in Table 3. The U1 site has a coordination environment similar to the U atoms in $UCl_4(POCl_3)$. The O atom occupies an equatorial position of the pentagonal bipyramid, and Cl atoms occupy the remaining sites. The U1–O distance of 2.366(7) Å may again be compared with the distances in $UClPO_4{\cdot}2H_2O$.[26] The U1–Cl_{ax} distances are 2.510(2) and 2.524(2) Å, and the Cl–U1–Cl angle is 171.04(8)°. U1–Cl_{eq} distances are 2.748(1) and 2.792(1) Å, consistent with those seen in $U_2O_2Cl_5$.[17] The U2–Cl distances range from 2.682(1) to 2.897(2) Å, consistent with the range of distances for the eight-coordinate U atoms in UCl_4[45] of 2.644–2.889 Å. The P–O distance of 1.460(7) Å is consistent with those for $[PO_2Cl_2]$ units,[42] and the P–Cl distances of 1.954(2) and 1.967(4) Å are slightly longer than those for $[PCl_4][SbF_6]$.[43]

Ab Initio Calculations. $U_2Cl_8(POCl_3)$ and $UCl_3(PO_2Cl_2)$ are found to be ferromagnetic, whereas $UCl_4(POCl_3)$ is found to be antiferromagnetic. From their respective total density of states at the Fermi level (see upper plots in Figures 13−15), one finds that $U_2Cl_8(POCl_3)$ is a strong metal, whereas $UCl_3(PO_2Cl_2)$ is a weaker metal. In contrast, $UCl_4(POCl_3)$ has a finite band gap, with a value of 0.35 eV. This value is probably slightly underestimated because of the well-known problem of the generalized gradient approximation[38] with excited states, although the nature of the material (metallic, semiconducting, or insulating) is usually given correctly.

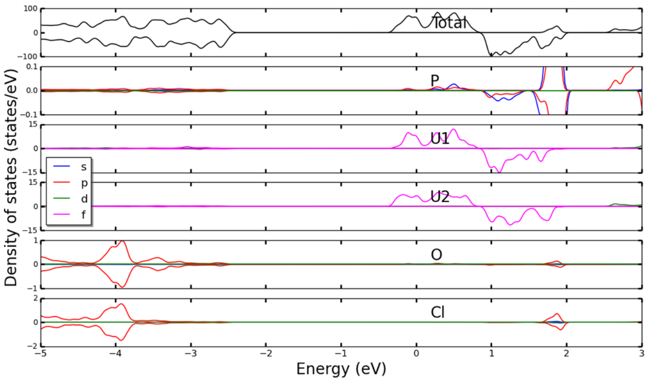

Figure 13. Density of states for $U_2Cl_8(POCl_3)$.

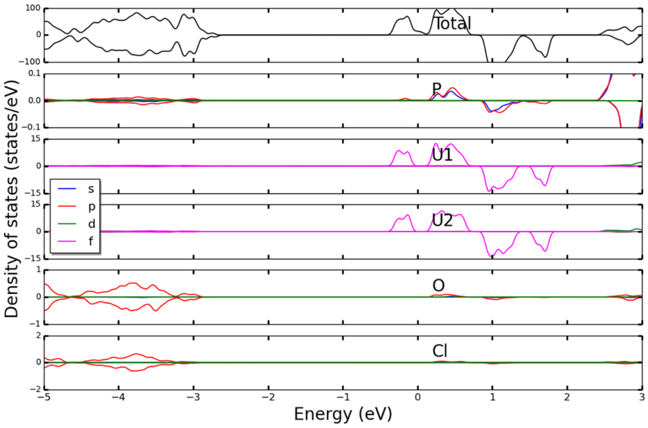

Figure 14. Density of states for $UCl_3(PO_2Cl_2)$.

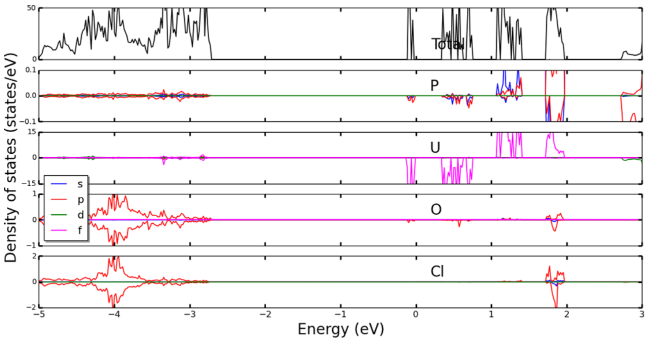

Figure 15. Density of states for $UCl_4(POCl_3)$.

From the lower plots of Figures 13−15 (corresponding to partial density of states), we observe that the states around the Fermi level (put at 0 eV) correspond to U-f states. However, at lower and at higher energies, all the species contribute to the electronic structures of the different compounds. The two crystallographically inequivalent U atoms in $UCl_3(PO_2Cl_2)$ show very similar partial density of states that are different from those of $U_2Cl_8(POCl_3)$. Also, the magnetic moment carried by the U atoms induces a small magnetization on the other species, as seen on their corresponding partial density of states, which are not symmetric for the up and down spin channels.

■ CONCLUSIONS

A series of chlorophosphate compounds of uranium(IV) have been obtained from solid-state reactions. The compounds $UCl_4(POCl_3)$ and $[U_2Cl_9][PCl_4]$ have been synthesized by the solid-state reactions of U, P_2O_5, and PCl_5 at 648 K; the compounds $UCl_3(PO_2Cl_2)$, and $U_2Cl_8(POCl_3)$ have been synthesized at 648 K with the same reactants plus added S.

$UCl_4(POCl_3)$ has an infinite chainlike structure with each U atom coordinated by six Cl atoms and one O atom in a pentagonal-bipyramidal arrangement. Each P atom within the structure is coordinated tetrahedrally by three Cl atoms and one O atom. The O atom is corner-shared with the U atom, and the three Cl atoms are terminal. $[U_2Cl_9][PCl_4]$ is a salt. Its structure is made up of infinite $[U_2Cl_9]$ sheets separated by $[PCl_4]$ units. Each U atom in $[U_2Cl_9][PCl_4]$ is seven-coordinate in a pentagonal-bipyramidal arrangement. The structure of $UCl_3(PO_2Cl_2)$ is three-dimensional and consists of infinite U/Cl chains linked together by $[PO_2Cl_2]$ units. The U atoms are seven-coordinate with two O atoms and five Cl atoms in a pentagonal-bipyramidal arrangement. The O atoms within the bipyramid occupy one of the axial positions and one of the equatorial positions. This differs from the commonly observed uranyl ion (UO_2^{2+}), in which O atoms occupy both of the axial positions. The structure of $U_2Cl_8(POCl_3)$ is made up of close-packed infinite sheets. There are two types of U atoms in the structure. One is coordinated by one O atom and six Cl atoms in a pentagonal-bipyramidal arrangement, and the other is coordinated by eight Cl atoms in a dodecahedron.

Ab initio calculations have been performed with density functional theory. The exchange-correlation potential was described at the generalized gradient approximation level including spin polarization. $U_2Cl_8(POCl_3)$ and $UCl_3(PO_2Cl_2)$ are found to be ferromagnetic, whereas $UCl_4(POCl_3)$ is found to be antiferromagnetic. $U_2Cl_8(POCl_3)$ is a strong metal, whereas $UCl_3(PO_2Cl_2)$ is a weaker metal. In contrast, $UCl_4(POCl_3)$ has a finite band gap, with a value of 0.35 eV. The density of states around the Fermi level correspond to U-f states. However, at lower and at higher energies, all the species contribute to the electronic structures of the different compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic file in CIF format for $UCl_4(POCl_3)$, $[U_2Cl_9][PCl_4]$, $UCl_3(PO_2Cl_2)$, and $U_2Cl_8(POCl_3)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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