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Syntheses, structures, and magnetic and optical properties of the compounds $[Hg_3Te_2][UCl_6]$ and $[Hg_4As_2][UCl_6]$

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ABSTRACT

Two new quaternary salts, $[Hg_3Te_2][UCl_6]$ and $[Hg_4As_2][UCl_6]$, have been synthesized and their structures determined by single-crystal X-ray diffraction analysis. $[Hg_3Te_2][UCl_6]$ is the product of a reaction involving UCl_4, $HgCl_2$, and HgTe at 873 K. The compound crystallizes in space group $P2_1/c$ of the monoclinic system. $[Hg_4As_2][UCl_6]$ results from the reaction of U, Hg_2Cl_2, and As at 788 K. It crystallizes in space group *Pbca* of the orthorhombic system. $[Hg_3Te_2][UCl_6]$ has a two-dimensional framework of $^2_\infty[Hg_3Te_2^{2+}]$ layers, whereas $[Hg_4As_2][UCl_6]$ has a three-dimensional framework of $^2_\infty[Hg_3As_2]$ layers interconnected by Hg atoms linearly bonded to As atoms. Both framework structures contain discrete $[UCl_6]^{2-}$ anions between the layers. $[Hg_3Te_2][UCl_6]$ exhibits temperature-independent paramagnetism. The optical absorption spectra of these compounds display *f–f* transitions.

1. Introduction

The vast majority of uranium transition-metal chalcogenides (S, Se, or Te) or pnictides (P, As, Sb, or Bi) whose structures are known incorporate 3*d* or 4*d* transition metals. The few with 5*d* transition metals that have been studied by single-crystal X-ray diffraction methods include $Cs_8Hf_5UTe_{30.6}$ [1], $Ir_2U_6Se_{15.5}$ [2], HfU_3Sb_5 [3], and $AuUSb_2$ [4]. To probe 5*d*/5*f* systems, we have chosen the Hg/U system for which the binary phase diagram [5] reveals only the phases $Hg_{45}U_{11}$, Hg_3U, Hg_2U, and HgU. We have probed this system with the use of mercury halides as reagents. These reagents have been shown to react with metals and chalcogens or pnictogens to produce quaternary compounds, most of which are nothing more than salts but most of which have been described as "supramolecular compounds". The chemistry of such compounds is rich and includes $[Hg_3Q_2][SiF_6]$ ($Q = $ S, Se, Te) [6], $[Hg_3Q_2][MX_6]$ ($Q = $ S, Se; $M = $ Zr, Hf; $X = $ Cl, Br) [7], $[Hg_3Se_2][Se_2O_5]$ [8], $[Hg_6T_4][MX_6]X$ ($T = $ P, As; $M = $ Mo, Ti; $X = $ Cl, Br) [9,10], $[Hg_7As_4][AgI_3]_2$ [11], $[Hg_3T_2][TlX_3]$ ($T = $ As, Sb; $X = $ Cl, Br) [12], $[Hg_6As_4][YbBr_6]Br$ [13], $[Hg_{11}As_4][GaBr_4]_4$ [14], and $[Hg_2As]_2[CdI_4]$ [15]. Here we report the syntheses, crystal structures, optical properties, and magnetic properties of the first Hg/U chalcogenides or pnictides, namely $[Hg_3Te_2][UCl_6]$ and $[Hg_4As_2][UCl_6]$.

2. Experimental

2.1. Syntheses

CCl_4 was dried over KH and distilled. UCl_4 was prepared by a modification of the literature procedure [16]. A 6.02 g (21.0 mmol) portion of UO_3 (Kerr-McGee Nuclear Corp.) was combined with 14.85 mL (105.3 mmol) of hexachloropropene (Aldrich, 96%) in a 150 mL round-bottom flask. The flask was fit with a condenser and placed under an N_2 atmosphere that was vented through a KOH bubbler. The N_2 had been passed over BASF catalyst at 353 K and then over Drierite to remove O_2 and H_2O. The flask was gradually heated to 403 K. This initiated an exothermic reaction that turned the solution into a deep-red color and released Cl_2 gas. Once the reaction was complete, the reaction mixture was allowed to reflux at 431 K for 3.5 h. The resulting green UCl_4 was separated from the solution by filtration through a cannula. Three successive washes of the product with 10 mL portions of CCl_4 were carried out. Residual CCl_4 was removed under vacuum.

Finely divided uranium powder was prepared by a modification of the literature procedure [17]. Uranium metal turnings (depleted, Oak Ridge National Laboratory) were washed with concentrated HNO_3 to remove any uranium oxide coating. The turnings were then rinsed with de-ionized water and dried with acetone. The uranium metal turnings were placed in a Schlenk vessel and reacted with an atmosphere of H_2 at 723 K to produce UH_3. UH_3 was converted to finely divided U powder under vacuum at 773 K.

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The remaining reactants were used as obtained. Reactions were carried out in fused-silica tubes. The tubes were charged with reaction mixtures under an Ar atmosphere in a glove box and then they were evacuated to $\sim 10^{-4}$ Torr and flame sealed. Selected single crystals from each reaction were examined with an EDX-equipped Hitachi S-3400 SEM. The compounds are both moderately stable in air.

2.2. Synthesis of $[Hg_3Te_2][UCl_6]$

The reaction mixture consisted of UCl_4 (0.11 mmol), HgTe (0.22 mmol; Aldrich Chemical Co.), and $HgCl_2$ (0.11 mmol; Mallinckrodt, Inc.). The reaction mixture was heated to 1123 K in 24 h, kept at 1123 K for 96 h, cooled at 6.8 K/h to 473 K, and then cooled rapidly to 293 K. Green plates of $[Hg_3Te_2][UCl_6]$ in about 70% yield were the major product, and green needles of UCl_4 were the minor product. In an alternative heating procedure, the reaction mixture was heated to 873 K in 15 h, kept at 873 K for 120 h, and then the furnace was turned off. This synthesis produced larger crystals of $[Hg_3Te_2][UCl_6]$ suitable for further measurements. EDX analysis of the green crystals showed the presence of Hg, Te, U, and Cl.

2.3. Synthesis of $[Hg_4As_2][UCl_6]$

We have prepared single crystals of $[Hg_4As_2][UCl_6]$ by the reaction of U (0.13 mmol), Hg_2Cl_2 (0.38 mmol; Alfa), and As (0.51 mmol; Strem Chemicals, Inc., 2N). The sample was heated to 788 K in 12 h, kept at 788 K for 144 h, and then the furnace was turned off. The product consisted of red blocks of $[Hg_4As_2][UCl_6]$ in about 80% yield. EDX analysis of the crystals showed the presence of Hg, As, U, and Cl.

2.4. Structure determinations

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [18]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of the data collection. Data were collected by a scan of 0.3° in ω in groups of 606 frames at φ settings of 0°, 90°, 180°, and 270°. The exposure times for $[Hg_3Te_2][UCl_6]$ and $[Hg_4As_2][UCl_6]$ were 30 and 25 s/frame, respectively. The collection of intensity data was carried out with the program SMART [18]. Cell refinement and data reduction were carried out with the use of the program APEX2 [19]. A Leitz microscope equipped with a calibrated traveling micrometer eyepiece was employed to measure accurately the crystal dimensions; face-indexed absorption corrections were performed numerically with the use of the program XPREP [20]. Then the program SADABS [18] was employed to make incident beam and decay corrections. The structures were solved with the direct methods program SHELXS and refined with the full-matrix least-squares program SHELXL [20]. Each final refinement included anisotropic displacement parameters. The program STRUCTURE TIDY [21] was used to standardize the positional parameters. Additional experimental details are given in Table 1 and the Supporting material. Selected metrical details are presented in Tables 2 and 3.

2.5. Magnetic susceptibility measurement

DC magnetic measurements of $[Hg_3Te_2][UCl_6]$ were carried out with the use of a Quantum Design MPMS5 SQUID magnetometer. Twenty-seven milligrams of ground single crystals were loaded into a gelatin capsule. Both zero-field cooled (ZFC) and field-cooled (FC) measurements were made between 2 and 400 K with a measuring field of 500 G. All data were corrected for electron core diamagnetism [22].

Table 1
Crystal data and structure refinements for $[Hg_3Te_2][UCl_6]$ and $[Hg_4As_2][UCl_6]$[a]

	$[Hg_3Te_2][UCl_6]$	$[Hg_4As_2][UCl_6]$
Fw	1307.70	1402.93
Space group	$P2_1/c$	$Pbca$
Z	2	8
a (Å)	6.835(1)	13.316(1)
b (Å)	7.864(1)	13.636(1)
c (Å)	13.632(2)	16.853(2)
β (°)	91.530(2)	90
V (Å^3)	732.4(2)	3060.0(5)
ρ_c (g/cm^3)	5.929	6.090
μ (cm^{-1})	473.2	558.5
$R(F)$[b]	0.038	0.033
R_w (F^2)[c]	0.109	0.083

[a] For both structures, $T = 153(2)$ K and $\lambda = 0.71073$ Å.
[b] $R(F) = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.
[c] For $F_o^2 < 0$, $w^{-1} = \sigma^2(F_o^2)$; for $F_o^2 \geqslant 0$, $w^{-1} = \sigma^2(F_o^2) + (0.0501 \times P)^2 + 33.397 \times P$ ($[Hg_3Te_2][UCl_6]$); $w^{-1} = \sigma^2(F_o^2) + (0.0197 \times P)^2 + 133.94 \times P$ ($[Hg_4As_2][UCl_6]$); $P = (F_o^2 + 2 \times F_c^2)/3$.

Table 2
Selected interatomic distances (Å) and angles (deg) for $[Hg_3Te_2][UCl_6]$[a]

U–Cl(1) × 2	2.622(3)
U–Cl(2) × 2	2.623(3)
U–Cl(3) × 2	2.624(3)
Hg(1)–Te	2.664(1)
Hg(1)–Te	2.666(1)
Hg(2)–Te × 2	2.672(1)
Cl–U–Cl	180
Cl(1)–U–Cl(2) × 2	88.20(10)
Cl(1)–U–Cl(3) × 2	88.35(10)
Cl(2)–U–Cl(3) × 2	89.06(10)
Te–Hg(1)–Te	172.82(2)
Te–Hg(2)–Te	180
Hg(1)–Te–Hg(1)	95.48(3)
Hg(1)–Te–Hg(2)	94.64(3)
Hg(1)–Te–Hg(2)	96.35(3)

[a] U and Hg(2) have crystallographic site symmetry $\bar{1}$.

Table 3
Selected interatomic distances (Å) and angles (deg) for $[Hg_4As_2][UCl_6]$

U–Cl(1)	2.605(3)	Cl(2)–U–Cl(6)	86.4(1)
U–Cl(2)	2.620(3)	Cl(3)–U–Cl(4)	92.1(1)
U–Cl(3)	2.624(3)	Cl(3)–U–Cl(5)	93.1(1)
U–Cl(4)	2.625(3)	Cl(3)–U–Cl(6)	90.1(1)
U–Cl(5)	2.629(3)	Cl(4)–U–Cl(5)	90.5(1)
U–Cl(6)	2.639(3)	Cl(4)–U–Cl(6)	177.8(1)
Hg(1)–As(1)	2.480(1)	Cl(5)–U–Cl(6)	89.8(1)
Hg(1)–As(2)	2.480(1)	As(1)–Hg(1)–As(2)	161.51(4)
Hg(2)–As(1)	2.467(1)	As(1)–Hg(2)–As(2)	175.73(4)
Hg(2)–As(2)	2.469(1)	As(1)–Hg(3)–As(2)	175.67(4)
Hg(3)–As(1)	2.462(1)	As(1)–Hg(4)–As(2)	167.96(4)
Hg(3)–As(2)	2.464(1)	Hg(1)–As(1)–Hg(2)	118.98(5)
Hg(4)–As(1)	2.485(1)	Hg(1)–As(1)–Hg(3)	108.41(4)
Hg(4)–As(2)	2.481(1)	Hg(1)–As(1)–Hg(4)	103.59(4)
		Hg(2)–As(1)–Hg(3)	107.32(4)
Cl(1)–U–Cl(2)	90.2(1)	Hg(2)–As(1)–Hg(4)	111.66(5)
Cl(1)–U–Cl(3)	179.3(1)	Hg(3)–As(1)–Hg(4)	106.19(5)
Cl(1)–U–Cl(4)	88.6(1)	Hg(1)–As(2)–Hg(2)	117.86(5)
Cl(1)–U–Cl(5)	86.6(1)	Hg(1)–As(2)–Hg(3)	108.76(4)
Cl(1)–U–Cl(6)	89.3(1)	Hg(1)–As(2)–Hg(4)	106.91(4)
Cl(2)–U–Cl(3)	90.0(1)	Hg(2)–As(2)–Hg(3)	102.82(4)
Cl(2)–U–Cl(4)	93.2(1)	Hg(2)–As(2)–Hg(4)	106.57(4)
Cl(2)–U–Cl(5)	175.1(1)	Hg(3)–As(2)–Hg(4)	114.19(5)