(EFG's) on the iodide ions are very nearly the same for all four components. ThI_4 and UI_4 have a monoclinic structure with the Ac^{4+} ion (Ac = actinide) in an 8-coordinate, distorted square antiprism with an $Ac^{4+}-I^-$ distance of 3.2 Å;[9] the β-PuBr$_3$ structure of NpI_3 and PuI_3 has the Ac^{3+} ion in a bicapped trigonal prism with $Ac^{3+}-I^-$ distances of about 3.3 Å.[10] Apparently, the EFG's from both structures are not sufficiently different to show any effect on the Mössbauer parameters.

PuI_3 becomes ferromagnetic at 4.75 K,[11] and a magnetic broadening of the Mössbauer spectra might be expected at lower temperatures. However, no difference could be determined between the spectra measured at 4.2 K and spectra measured at temperatures above 4.75 K.

The [129]I Mössbauer parameters of the actinide iodides are the result of covalent contributions to the largely ionic bonding in these compounds and offer a measure of the covalency in their bonding. A combination of theoretical considerations[12] and empirical correlations from the [129]I Mössbauer parameters of a large number of iodine-containing compounds[6,13] can be used to calculate the hole population (h_p) for each of the three 5p orbitals. The expressions used in the calculations are

$$\delta \text{ (mm/s)} = 1.5h_p - 0.54 \qquad (4)$$

where 0.54 mm/s is the empirically determined shift[13] for pure unhybridized σ-bonds and h_p, the hole population, is

$$h_p = h_{p_x} + h_{p_y} + h_{p_z} \qquad (5)$$

The reduced quadrupole coupling constant, U_p, is defined by

$$U_p = eq_{zz}^{mol}/eq^{at} = h_{p_z} - (h_{p_x} + h_{p_y})/2 \qquad (6)$$

and the asymmetry of the EFG is given by

$$\eta^{mol} = (h_{p_x} - h_{p_y})/(h_{p_z} - h_p/3) \qquad (7)$$

The quadrupole coupling constant, e^2Q_{129}/h, is converted to Q_{127} units by multiplying by 31.90 MHz/(mm/s); in these units, $eq^{at} = 2293$ MHz.

The parameters of Table II all fall into a rather narrow range, and thus, the estimates of hole populations will be very nearly the same. Instead of values being calculated for each compound, the parameters for all four compounds were averaged and the hole populations calculated from the averaged parameters. These are $\delta = 0.285$ mm/s, $e^2qQ_{127}/h = -285$ MHz, and $\eta = 0.40$. The calculated values for h_p, h_{p_z}, h_{p_x}, and h_{p_y} are 0.55, 0.27, 0.15, and 0.12 mm/s, respectively.

These hole populations are approximately $h_{p_x} \simeq h_{p_y} \simeq 0.5h_{p_z}$, which is the condition for an axially symmetric field with bonding along the z axis. The h_{p_z} value implies about 13% covalency in the bonding. The [237]Np Mössbauer spectrum of NpI_3 shows an isomer shift slightly negative relative to that of $NpCl_3$,[14] which implies that no appreciable electron density from the iodide ions is contributed to the 5f orbitals that shield the 6s orbitals of Np^{3+}. The iodide contribution to the Np^{3+} ion is not into the 5f orbitals, but into Np 6p or Np 6d orbitals. As the 6p orbitals are filled, a contribution to the 6d orbitals appears more likely. Theoretical calculations[16] suggest that ligand contributions to 6d orbitals are to be expected in actinide bonding.

A comparison of these results with those of da Costa et al.[1,2] on LaI_3, GdI_3, and ErI_3 shows an unexpected difference in the

isomer shifts. For the lanthanide iodides, da Costa et al. found δ of ~-0.25 mm/s, compared to the +0.25 and 0.35 mm/s values found for NpI_3 and PuI_3 in this work. The Ln^{3+} ions range in ionic radii from 1.06 to 0.88 Å, while Np^{3+} and Pu^{3+} have ionic radii of 1.04 and 1.00 Å, respectively.[15] NpI_3, PuI_3, and LaI_3 all have the β-PuBr$_3$ crystal structure. The 5f ions show more tendency toward covalent contribution to their bonding, but it is surprising that it would be reflected by a 0.5 mm/s difference in δ.[17]

The quadrupole coupling constants for LnI_3 were found to be -100 MHz, compared to the average of -285 MHz for AcI_3 or AcI_4; both are very small and appear to show a reasonable 4f-5f difference. The agreement in the asymmetry parameters is as good as could be expected. It should be noted that da Costa et al.[2] did not have available the latest values of the empirical constants,[6,13] which might change some of their values, but not enough to affect the comparisons drawn here.

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(17) The author has discarded a suggestion that the negative values for LnI_3 were caused by measurements in the Southern Hemisphere.

Contribution from the Departamento de Química Inorgánica,
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Dimethyl(2-thiouracilato)thallium(III), a Compound with an Unusual C-Tl-C Angle[1]

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The cation dimethylthallium(III) (Me_2Tl^+) is one of the most stable methylated species in aqueous solution.[3] There is evidence[4] that it may be formed from thallium(I) by biomethylation. Its toxicology has not been sufficiently investigated as to enable estimates of its environmental impact to be made, present knowledge suggesting that although it is as toxic as methylmercury(II) for microorganisms,[5] it has little effect on rats.[6] Its coordination chemistry in the solid state has been studied by X-ray diffraction in a relatively small number of compounds,[7,8] in all of which the C-Tl-C group is linear or near-linear, the angle varying from 163.5 (9) to 180°.

In the course of our studies on the coordination chemistry of organometallic cations formed by complexation of mercury(II) or thallium(III) with organic molecules capable of assuming different tautomeric forms, we have investigated the reaction between Me_2Tl^+ and the ligand 2-thiouracil (H_2Tu) in basic media. X-ray diffraction studies of the product, $Me_2Tl(HTu)$,

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Table I. Final Positional Coordinates and Equivalent Isotropic Thermal Parameters with Standard Deviations in Parentheses

atom	x/a	y/b	z/c	$B,^a$ $Å^2$
Tl	0.3663 (1)	0.25	0.3553 (1)	3.71 (3)
S	0.6916 (9)	0.0558 (9)	0.414 (1)	3.4 (2)
O	1.195 (4)	0.151 (3)	1.006 (4)	5.9 (6)
N(1)	0.650 (2)	0.242 (5)	0.655 (2)	2.9 (4)
N(3)	0.950 (3)	0.120 (3)	0.743 (3)	3.1 (4)
C(2)	0.768 (4)	0.144 (3)	0.624 (4)	3.4 (5)
C(4)	1.014 (6)	0.184 (4)	0.907 (5)	4.8 (7)
C(5)	0.900 (4)	0.289 (3)	0.952 (4)	4.1 (6)
C(6)	0.724 (4)	0.327 (3)	0.818 (4)	3.7 (5)
Cm_1	0.149 (5)	0.367 (4)	0.468 (5)	4.9 (7)
Cm_2	0.504 (7)	0.395 (5)	0.199 (7)	7 (1)

^{a} For Tl and S atoms $B_{eq} = {}^4/_3\sum_{ij}B_{ij}(a_ia_j)$.

have shown that in this compound the C-Tl-C angle is 106 (1)° and that HTu is coordinated via one of its nitrogen atoms and its sulfur atom and, intermolecularly, via its oxygen atom. As far as we know, this is the first time that this coordination pattern has been established for HTu on X-ray diffraction grounds.

Experimental Section

Me$_2$Tl(HTu) was prepared by reacting H$_2$Tu (EGA-Chemie) in methanol with an equimolar quantity of Me$_2$TlOH obtained in aqueous solution by treating Me$_2$TlI[9] with freshly precipitated Ag$_2$O. After several hours of stirring, the white crystalline precipitate was filtered off and dried in vacuo over P$_4$O$_{10}$.[10] The infrared spectrum was recorded as a Nujol mull and KBr disk on a Perkin-Elmer 180 spectrometer, the Raman spectrum was obtained on a Jarrell-Ash 500 spectrometer (argon ion laser, 5145 Å), and ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM250 apparatus (DMSO-d_6 solutions).

X-ray Diffraction Data. An Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used to get the necessary information from a prismatic crystal of approximate dimensions 0.05 × 0.12 × 0.25 mm. Unit cell parameters were obtained by least squares on setting angles of 15 reflections in the range $18 < 2\theta < 35°$. Reflections were measured at 296 K by the ω-2θ scan technique with scan widths $(0.60 + 0.35 \tan \theta)°$ and a maximum scan speed of 6.7° min^{-1}; the hkl range was $-10 < h < 10$, $k < 14$, and $l < 11$, and the maximum θ value was 30°. From 1883 reflections measured, 1447 were unique, with $R_{sym} = 0.025$ after absorption correction (transmission factors 0.66–0.14). The standard reflection 004 varied ±1% of the mean intensity over the course of data collection. Data were corrected for Lorentz and polarization effects.

Results and Discussion

Crystal Structure. The crystals are monoclinic, space group $P2_1$, with $a = 6.815$ (2) Å, $b = 9.745$ (6) Å, $c = 7.298$ (1) Å, $\beta = 103.71$ (2)°, $V = 471$ (1) Å^3, $Z = 2$, $D_{calcd} = 2.55$ g cm^{-3}, μ(Mo Kα) = 16.7 mm^{-1}, $F(000) = 328$ electrons, and $T = 296$ K.

The structure was solved by standard Patterson and Fourier methods. Refinement was carried out by using the 823 reflections with $I > 3\sigma(I)$ (also excluding 001, 012, and $\bar{1}$11), minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + 0.001F_o^2]$. In final least-squares cycles, Tl and S atoms were treated anisotropically. A total of 56 parameters were refined, including one for secondary extinction defined by $F_{cor} = F_c/[1 - \chi F_c^2/\sin \theta]$, which converged to $\chi = 6.8 \times 10^{-7}$. The refinement was stopped when $\Delta/\sigma = 0.01$; at that stage the R factors were $R = 0.052$ and $R_w = 0.054$. Refinement of the enantiomorph model obtained by reversing all atomic coordinates converged to the same R_w value. The absolute chirality of the molecule could not therefore be obtained by this often straightforward procedure.[11] A final difference map showed fluctuations between −2.5 and +2.1 e Å^{-3}. Scattering factors were taken from Cromer and Waber[12] and corrections for anomalous dispersion from Cromer and Ibers.[13]

**Table II.** Interatomic Bond Distances (Å)^a

Tl–S	2.869 (8)	N(1)–C(2)	1.30 (5)
Tl–N(1)	2.55 (2)	N(1)–C(6)	1.44 (4)
Tl–Cm_1	2.18 (4)	N(3)–C(2)	1.36 (4)
Tl–Cm_2	2.16 (5)	N(3)–C(4)	1.33 (4)
Tl–O^i	2.72 (3)	C(4)–C(5)	1.37 (5)
S–C(2)	1.73 (3)	C(5)–C(6)	1.41 (4)
O–C(4)	1.31 (5)		

^{a}O^i obtained from O by $-1 + x$, y, $-1 + z$.

Table III. Interatomic Bond Angles (deg)^a

S–Tl–N(1)	56.7 (7)	Cm_2–Tl–O^i	83 (1)
S–Tl–Cm_1	149 (1)	C(2)–N(1)–C(6)	117 (1)
S–Tl–Cm_2	95 (1)	C(2)–N(3)–C(4)	123 (1)
S–Tl–O^i	92.9 (6)	S–C(2)–N(1)	117 (1)
N(1)–Tl–Cm_1	98 (1)	S–C(2)–N(3)	121 (1)
N(1)–Tl–Cm_2	98 (1)	O–C(4)–N(3)	116 (1)
N(1)–Tl–O^i	149.6 (9)	O–C(4)–C(5)	124 (1)
Cm_1–Tl–Cm_2	106 (1)	C(4)–C(5)–C(6)	118 (1)
Cm_1–Tl–O^i	111 (1)	N(1)–C(6)–C(5)	120 (1)

^{a}O^i obtained from O by $-1 + x$, y, $-1 + z$.
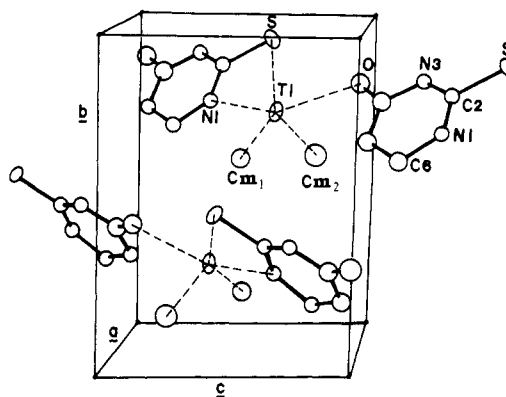
Figure 1. Structure of the Me$_2$Tl(HTu) molecule.

Most calculations were performed on a VAX computer with the SHELX76[14] system of programs and ORTEP.[15]

The scattering is heavily dominated by the Tl atom. In fact, anisotropically refined structure factors calculated from only this atom render an R factor of 0.10. This fact causes a rather low accuracy in the final fractional coordinates and consequently also in the calculated bond distances and angles. The final difference map shows fluctuations of about ±2 e Å^{-3}, all of which are about 1 Å from the heavy atom. They were ascribed to limited accuracy in the absorption corrections due to the poorly defined shape of the crystal.

Final positional parameters and equivalent temperature factors calculated according to Hamilton[16] are given in Table I. Interatomic bond distances and angles are given in Tables II and III, respectively.

The Tl atom is coordinated to the two methyl carbons, to the sulfur and one nitrogen atom of one thiouracil group, and to the carbonyl oxygen of another thiouracil related to the first by unit cell translation along a and c. The coordination number is therefore 5, and the coordination polyhedron may be described as a rather distorted square pyramid with its base defined by the S, N(1), Cm_1 and O atoms and its apex by Cm_2.

Although the C-Tl-C angle of the Me$_2$Tl$^+$ group is much more acute than in any of this cation's compounds that have been studied hitherto, the distances d(Tl-C) are quite normal.[7,8] The distances d(Tl-N), d(Tl-S), and d(Tl-O) in Figure 1 are all appreciably shorter than the sums of the van der Waals radii,[17] but these bonds

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probably differ in strength. The Tl–N bond length is similar to that observed in (Me₂TlPhen)⁺ [18] and Me₂Tl(L-PHE)[19a] and shorter than in the other N-bonded compounds that have been studied,[8,19b] suggesting this to be a relatively strong bond. The distance d(Tl–S) is intermediate between the two d(Tl–S) distances in Me₂TlSC₆H₅,[20] in which the sulfur forms asymmetrical Tl–S–Tl bridges, and decidedly shorter than in Me₂TlS₂COCH₃,[21] a relatively stable bond again being indicated. The length of the Tl–O bond, on the other hand, is considerably greater than in other compounds,[19,20] falling within the range considered appropriate for weak bonds in complexes of dimethylthallium(III) with polydentate ligands.[8] The structure of the ligand differs considerably from that of free H₂Tu, which in the solid state adopts the lactam–thione form.[22] Loss of a proton and combination with Me₂Tl⁺ brings about a lengthening of the C–O and C–S bonds, though without their reaching values corresponding to single bonds (1.50 and 1.79 Å, respectively[23]). These changes suggest the following charge distribution in the dimethylthallium(III) compound:
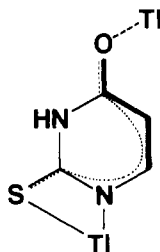
Vibrational and NMR Spectra. In the vibrational spectra the wavenumbers of the significant stretching vibrations of the complexed ligand[24] agree with the kind of coordination described above. With respect to the free ligand, the bands corresponding to stretching of the ring or the thioamide group remain unchanged or shift to slightly higher wavenumbers, where as that band with the most ν(C═S) character shifts to lower wavenumbers.[25] The C–Tl–C stretching bands[26] appear very close together at wavenumbers lower than those reported for other systems, and two new bands that show up in the low-wavenumber region[27] may possess ν(Tl—O) and ν(Tl—S) contributions.

The compound Me₂Tl(HTu) is insoluble in water and in organic solvents of low dielectric constants but dissolves in DMF and DMSO. Its characteristics in DMSO-d_6 were investigated by using ¹H and ¹³C NMR and IR spectroscopy. The existence of bands attributable to ν(C═O) close to those found in the solid suggests the presence of the lactam form in solution, and the broad ¹H NMR band at 11.7 ppm[28] must accordingly be attributed to the nondeprotonated NH group. The ¹³C NMR signals appear at positions between those found in S-methylated and N-methylated 2-thiouracils,[29] except for the C(2) signal, which

practically coincides with the corresponding signal in the N-(1)-methylated derivative.[29] This may be due to the greater electron-accepting capacity of the thallium atom in the complex, which must have an unshielding effect tending to oppose the shielding caused by the ligand's partial change toward the thiol form. These NMR data suggest that in solution the ligand remains coordinated to the metal via the sulfur atom and one of the nitrogen atoms, but they offer no grounds for judging whether the C═O group takes part in the bond, and for reasons already mentioned it is unadvisable to base such a judgement upon the IR data.[25]

The methyl signals of the organometallic part of the complex appear in ¹H and ¹³C NMR spectra at 0.88 and 23.24 ppm, respectively. The coupling constants ²J(Tl–H) and ¹J(Tl–C) are 420 and 3033 Hz, respectively.[30] These values are not notably different from those reported for the other Me₂Tl⁺ complexes with sulfhydrylated ligands, in which the C–Tl–C group is practically linear.[31] If coupling takes place fundamentally via Fermi contact contribution[32] depending on the degree to which the thallium s orbitals participate in the bond, then the organometallic moiety of Me₂Tl(HTu) would appear to adopt a more open configuration in solution than in the solid state.

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(26) ν$_{asym}$ 510 s (IR), 507 m cm⁻¹ (R); ν$_{sym}$ 495 w (IR), 495 s cm⁻¹ (R).
(27) 295 w (IR), 293 m cm⁻¹ (R); 285 m cm⁻¹ (IR).
(28) Other signals in the ¹H and ¹³C NMR spectra (ppm from TMS): 5.71 d [H(5)] and 742 d [H(6)] ($J_{5,6}$ = 6.7 Hz); 176.8 [C(2)], 163.1 [C(4)], 106.3 [C(5)], and 150.8 [C(6)].

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Synthesis and Spectroscopic Characterization of the Purple Tris(phenanthrenequinone diimine)ruthenium(II) Ion

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There has been considerable attention focused on the optical and electronic properties of ruthenium(II) polypyridyl complexes and on their rich excited-state chemistry because of their possible application in the design of photochemical sensitizers for solar energy conversion.[1–3] The intense coloration and stability of the ruthenium(II) diimine complexes furthermore provide uniquely sensitive photophysical probes for solids, for surfaces, and, in our own laboratory, for biopolymers.[4,5] While the detailed characterization of the ground- and excited-state electronic structures of bipyridyl and phenanthroline complexes of ruthenium(II) has proceeded, little attention has been given to other diimine complexes of ruthenium(II). We have examined complexes of the phenanthrenequinone diimine ligand to explore new photochemical

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