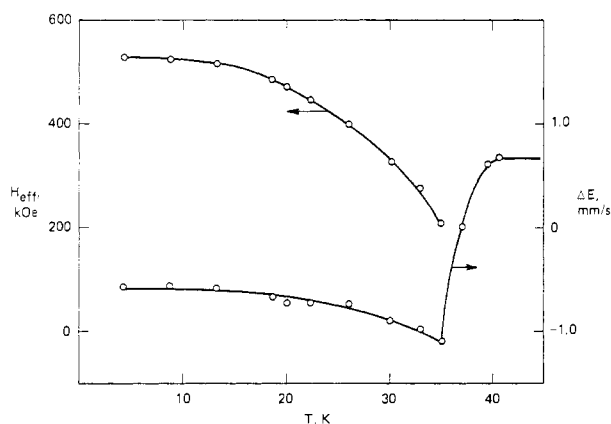


Table I. Mössbauer Parameters for MnFeF₅·2H₂O

temp, K	δ , mm/s ^a	ΔE , mm/s	H_{eff} , kOe
4.2	0.43	-0.58	527
8.66	0.44	-0.58	523
13.2	0.43	-0.60	514
18.6	0.45	-0.68	485
20.1	0.41	-0.75	470
22.2	0.45	-0.74	445
26.1	0.45	-0.75	398
30.3	0.40	-0.92	325
33.0	0.40	-0.99	276
35.0	0.44	-1.11	207
37.0		~0	180 ± 20 ^b
39.4	0.46	0.61	
40.5	0.48	0.69	
53	0.47	0.66	
RT	0.46	0.64	

^a Relative to α -iron. ^b Estimated.

**Figure 4.** Mössbauer parameters for MnFeF₅·2H₂O vs temperature.

slow relaxation.¹⁰⁻¹³ The model that qualitatively fits these spectra best is that of Hoy and Corson.¹⁴ Their model considers an insulator just above T_c as composed of paramagnetic regions and clusters of spins with small values of reduced magnetization. The spins in paramagnetic regions are fluctuating rapidly, and the spins of the cluster regions fluctuating more slowly. As the temperature is lowered, the relative amount of paramagnetic to spin clusters decreases until the paramagnetic component disappears (ca. 37 K for MnFeF₅·2H₂O) and is replaced by an ordered region with significant values of reduced magnetization. This ordered component increases relative to the spin clusters until at lower temperatures only the ordered component is shown by the spectrum (Figure 2).

The data for the ordered region are shown in Table I and Figure 4. The effective internal field, H_{eff} , increases smoothly with decreasing temperature to reach a value of 527 kOe at 4.2 K. The quadrupole-splitting constant, ΔE , is -0.58 at 4.2 K and slowly decreases to -1.1 at 35 K. Between 35.0 and 39.4 K, there is a virtual discontinuity as ΔE increases to its paramagnetic value of 0.65 mm/s as paramagnetism replaces ordering.

The H_{eff} values for the Fe³⁺ Mössbauer parameters of MnFeF₅·2H₂O are in excellent agreement with the Fe³⁺ Mössbauer parameters for Fe₂F₅·2H₂O determined by Walton et al.² and Imbert et al.⁶ At 4.2 K, the H_{eff} of 527 kOe for MnFeF₅·2H₂O may be compared with H_{eff} of 532 kOe² and 538 kOe⁶ determined for Fe₂F₅·2H₂O. At 20 K, the H_{eff} of 460 kOe² for Fe₂F₅·2H₂O

may be compared with 470 kOe determined for MnFeF₅·2H₂O in this study. The Mössbauer parameters for MnFeF₅·2H₂O do not show the transition below T_c found by Imbert et al.⁶ on a sample of Fe₂F₅·2H₂O prepared by dehydration of Fe₂F₅·7H₂O. Walton et al.² did not observe this transition on crystalline Fe₂F₅·2H₂O. The MnFeF₅·2H₂O samples in this work were prepared by the same procedure as that used by Walton et al.

The quadrupole-splitting constant of 0.65 mm/s for Fe³⁺ in MnFeF₅·2H₂O is essentially the same in the paramagnetic region of the spectrum as those reported for Fe³⁺ in Fe₂F₅·2H₂O, 0.65 and 0.59 mm/s.^{2,6,7} However, the ΔE for MnFeF₅·2H₂O in the ordered region is a factor of 6 greater than the ΔE of -0.105 mm/s found by Imbert et al.⁶ for Fe₂F₅·2H₂O in the same region. Presumably, this reflects the stronger crystal field from the Mn²⁺ (3d⁵) ion than from the Fe²⁺ (3d⁶) ion.

In general, this study shows the Fe³⁺ ion in MnFeF₅·2H₂O to have magnetic properties very similar to those of Fe³⁺ in Fe₂F₅·2H₂O. This result might clarify the problem of the saturation magnetization of MnFeF₅·2H₂O.⁵ The saturation magnetization of Fe₂F₅·2H₂O agrees nicely with a simple model for negative exchange, $\mu(\text{Fe}^{3+}) - \mu(\text{Fe}^{2+}) = 1.0 \mu_B$ vs the experimental 1.2 μ_B .² Substitution of Mn²⁺ for Fe²⁺ by the same model would lead to $\mu_B = 0$, rather than 1.1 μ_B found by Jones et al.⁵ The determination of this work that the Fe³⁺ ions in MnFeF₅·2H₂O and Fe₂F₅·2H₂O have very similar magnetic properties suggests that the agreement found for the simple model of negative exchange may be fortuitous; and a more complicated model, involving magnetic sublattices, may be required to be consistent with both compounds.¹⁵ The explanation for the differences in the T_c temperatures for MnFeF₅·2H₂O and Fe₂F₅·2H₂O may also lie with such a model.

Registry No. MnFeF₅·2H₂O, 66106-43-2.

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Iodine-129 Mössbauer Study of Actinide Iodides[†]

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The ¹²⁹I Mössbauer effect can provide information on the bonding characteristics of iodine-containing compounds. Previous studies^{1,2} investigated LaI₃, GdI₃, and ErI₃ and found a slight effect on the 5p electron distribution in these compounds. Four actinide iodides, ThI₄, UI₄, NpI₃, and PuI₃, were investigated in this study to compare with the lanthanide iodides.

Experimental Section

The compounds were prepared from ¹²⁹I obtained as an Na¹²⁹I solution from the Isotopes Division of Oak Ridge National Laboratory (ORNL). Hg¹²⁹I₂ was precipitated from solution, centrifuged, washed, and dried under vacuum for 2-3 days. Actinide iodides were prepared by reacting actinide metals with a 20% excess of Hg¹²⁹I₂ at 350-400 °C in evacuated, sealed glass tubes.³ Typical preparations used 20-30 mg of the actinide metal and 80-90 mg of Hg¹²⁹I₂.

The source for the Mössbauer study was an Mg₃¹²⁹TeO₆ pellet, prepared from enriched ¹²⁸Te by the Isotopes Division of ORNL and irradiated for 2 weeks in the ORNL HIFR reactor.⁴ Samples contained about 20 mg of the compound under study sealed between two layers of plastic.

[†] The information contained in this paper was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

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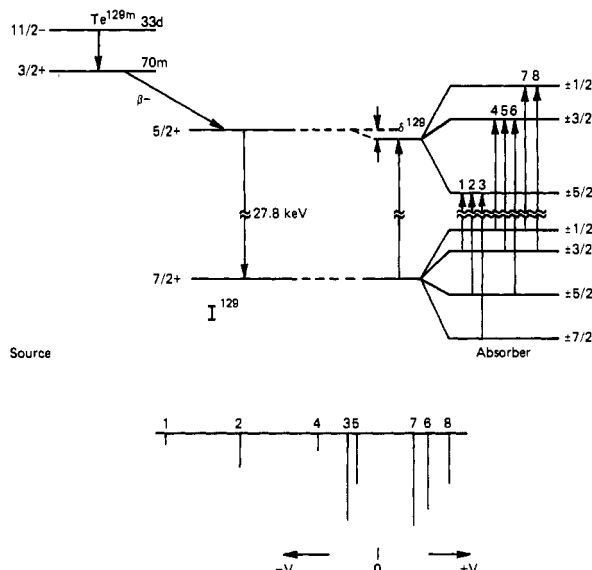


Figure 1. Nuclear energy levels for ^{129}Te source and ^{129}I absorber (eq assumed positive) and line positions in a ^{129}I Mössbauer spectrum.

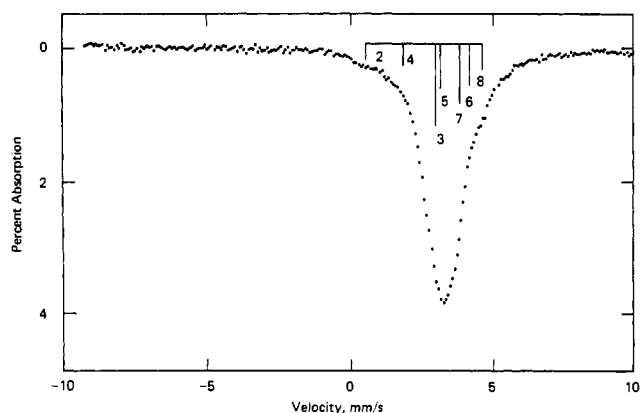


Figure 2. ^{129}I Mössbauer spectrum of $\text{Pu}^{129}\text{I}_3$. Bars represent relative intensities calculated from ref 7.

Mössbauer spectra were measured in vertical transmission geometry with an Austin Science Associates instrument operated in a constant-acceleration mode. Both source and sample were cooled to liquid-helium temperatures in a Janis Vari-Temp cryostat; the temperature was measured with a calibrated germanium resistance thermometer. Spectra were normally measured at temperatures in the range 7–15 K to minimize helium use.

The detector was an $\text{Na}(\text{Tl})\text{I}$ crystal; counting rates were of the order of 10^3 counts for each of the 512 channels. The velocity was calibrated with a ^{57}Co -Rh source and α -iron foil absorber replacing the ^{129}Te source and absorber. The correction to zero velocity for the ^{57}Co -Rh source was taken as -0.11 mm/s;⁵ correction from the $\text{Mg}_3^{129}\text{TeO}_6$ source to Zn^{129}Te was taken to be -3.49 mm/s.⁶ With these corrections the isomer shift of Cu^{129}I was measured as -0.44 mm/s, in reasonable agreement with the recommended value of -0.41 mm/s.⁶

Results and Discussion

The ^{129}I Mössbauer spectra of the actinide iodides all showed a single asymmetric resonance with inflections in the envelope.

Table I. Comparison of Assigned and Calculated Line Positions

transition	line position, ^a mm/s		transition	line position, ^a mm/s	
	assigned	calcd		assigned	calcd
2	1.67	1.63	6	4.99	4.88
3	3.54	3.52	7	4.56	4.65
4	2.86	2.90	8	5.41	5.40
5	3.71	3.75			av dev 0.05

^aRelative to $\text{Mg}_3^{129}\text{TeO}_6$ source.

Table II. Mössbauer Parameters of Actinide Iodides

compd	temp, K	IS, mm/s		e^2qQ_{127}/h , MHz	η^a	U_p^b
		measd	rel to Zn^{129}Te			
ThI_4	5.5	3.72	0.23	-310	0.36	0.14
U_4I_4	10	3.81	0.32	-280	0.54	0.12
NpI_3	8.5	3.73	0.24	-290	0.38	0.13
PuI_3	9	3.84	0.35	-260	0.32	0.11

^aThe asymmetry parameter. ^bThe reduced field gradient, $U_p = eq_{zz}^{\text{mol}}/eq_{zz}^{\text{at}}$.

The inflections and asymmetry of the envelope indicated that the normal ^{129}I quadrupole splitting was too small to be resolved.

The nuclear energy levels of the quadrupole-split ^{129}I Mössbauer spectrum and the line positions for the normal spectrum ($eq > 0$) are shown in Figure 1. Each half of a spectrum was analyzed by assigning transitions to inflection points in the envelope of the resonance. The transition positions for both halves were then averaged. The spectrum of PuI_3 and the transitions assigned are shown in Figure 2. The line energies from these assignments were least-squares fitted to the theoretical expression for each transition by the method of Shenoy and Dunlap.⁷

The energy of each nuclear level is represented by

$$E(I, I_z) = e^2QV_{zz} \sum_{N=0}^4 A_N(I, I_z) \eta^N \quad (1)$$

where E is the level energy for state I and level I_z , V_{zz} is the electric field gradient, $A_N(I, I_z)$ are the eigenvalue coefficients for state I and level I_z , η is the asymmetry parameter defined by

$$\eta = (V_{xx} - V_{yy})/V_{zz} \quad (2)$$

and Q is the nuclear quadrupole moment. The values of $A_N(I, I_z)$ are tabulated by Shenoy and Dunlap.⁷ The energy of a transition is the difference in the energies of level I^*, I_z^* and level I, I_z and is given by

$$R(I_z^*, I_z) = [E(I^*, I_z^*) - E(I, I_z)] + \delta \quad (3)$$

where R is the transition energy between the levels of the excited and ground states (see Figure 1) and δ is the isomer shift. The experimental transition energies were fitted to the theoretical expression to yield δ , the quadrupole coupling constants e^2qQ_{129}/h (by convention, converted to MHz for ^{127}I), and the asymmetry parameter (η) by a nonlinear, least-squares computer program.⁸ A comparison between the assigned transitions and calculated values for the PuI_3 spectrum is shown in Table I; the Mössbauer parameters for all four actinide iodides are presented in Table II.

The error in the Mössbauer parameters is interrelated by the computer program, but none of the values have a strong dependence on the fit. A reasonable estimate of the errors is ± 0.08 mm/s for δ , ± 30 MHz for the quadrupole coupling constant, and ± 0.1 for η , the asymmetry parameter.

The Mössbauer parameters are not significantly different among the four actinide iodides, implying that the electric field gradients

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(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 ($\text{Ac} = \text{actinide}$) in an 8-coordinate, distorted square antiprism with an $\text{Ac}^{4+}-\text{I}^-$ distance of 3.2 Å,⁹ the $\beta\text{-PuBr}_3$ structure of NpI_3 and PuI_3 has the Ac^{3+} ion in a bicapped trigonal prism with $\text{Ac}^{3+}-\text{I}^-$ 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 considerations¹² 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

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

where 0.54 mm/s is the empirically determined shift¹³ for pure unhybridized σ -bonds and h_p , the hole population, is

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

The reduced quadrupole coupling constant, U_p , is defined by

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

and the asymmetry of the EFG is given by

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

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, $eq^{\text{at}} = 2293$ 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_x} , h_{p_y} , and h_{p_z} are 0.55, 0.27, 0.15, and 0.12 mm/s, respectively.

These hole populations are approximately $h_{p_x} \cong h_{p_y} \cong 0.5h_{p_z}$, 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 calculations¹⁶ 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 $\beta\text{-PuBr}_3$ 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.

Registry No. ^{129}I , 15046-84-1; ThI_4 , 7790-49-0; UI_4 , 13470-22-9; NpI_3 , 15513-95-8; PuI_3 , 13813-46-2.

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

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Dimethyl(2-thiouracilato)thallium(III), a Compound with an Unusual C-Tl-C Angle¹

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The cation dimethylthallium(III) (Me_2Tl^+) is one of the most stable methylated species in aqueous solution.³ There is evidence⁴ 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, $\text{Me}_2\text{Tl}(\text{HTU})$,

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