

**Table M26-ii-001.** (NH<sub>4</sub>)<sub>2</sub>H<sub>3</sub>IO<sub>6</sub>, (ND<sub>4</sub>)<sub>2</sub>D<sub>3</sub>IO<sub>6</sub>. Fractional coordinates [ $\cdot 10^5$ ] and isotropic temperature parameters [80Tic].  $B_{\text{iso}}$  is calculated from  $\beta_{\text{ij}}$  defined by Eq. (c) in Introduction.

(NH <sub>4</sub> ) <sub>2</sub> H <sub>3</sub> IO <sub>6</sub>				
	$x$	$y$	$z$	$B_{\text{iso}} [\text{\AA}^2]$
I	0	0	0	0.33
O	21850(21)	−750(22)	9662(12)	0.63
N	0	0	35937(15)	1.15
H(1)	30118(88)	12492(97)	1481(47)	1.31
H(2)	0	0	27201(51)	4.28
H(3)	15620(47)	3842(53)	38720(30)	2.61
(NH <sub>4</sub> ) <sub>2</sub> D <sub>3</sub> IO <sub>6</sub>				
	$x$	$y$	$z$	$B_{\text{iso}} [\text{\AA}^2]$
I	0	0	0	0.53
O	21751(25)	−887(26)	9638(13)	0.80
N	0	0	35904(17)	1.36
D(1)	29935(56)	12471(57)	14781(30)	1.01
D(2)	0	0	26835(34)	4.34
D(3)	15876(32)	4225(34)	38808(17)	2.41

**Table M26-ii-002.** (NH<sub>4</sub>)<sub>2</sub>H<sub>3</sub>IO<sub>6</sub>, (ND<sub>4</sub>)<sub>2</sub>D<sub>3</sub>IO<sub>6</sub>. Interatomic distances [Å] and angles [°] [80Tic]. Bond lengths N–H were corrected for riding motion. All other bond lengths were corrected for independent vibration of atoms.

	(NH <sub>4</sub> ) <sub>2</sub> H <sub>3</sub> IO <sub>6</sub>		(ND <sub>4</sub> ) <sub>2</sub> D <sub>3</sub> IO <sub>6</sub>	
	Uncorrected	Corrected	Uncorrected	Corrected
IO <sub>6</sub> octahedron				
I–O	1.879(1)	1.887(1)	1.878(1)	1.889(1)
O...O <sup>iii</sup>	2.666(2)	2.673(2)	2.666(3)	2.674(3)
O...O <sup>iv</sup>	2.648(2)	2.655(2)	2.645(3)	2.653(3)
O–I–O <sup>iii</sup>	90.40(6)		90.45(6)	
O–I–O <sup>iv</sup>	89.60(6)		89.55(6)	
NH <sub>4</sub> tetrahedron				
N–H(2)	0.974(6)	1.034(6)	1.012(4)	1.067(4)
N–H(3)	1.024(3)	1.046(3)	1.039(2)	1.055(2)
H(2)...H(3)	1.613(5)	1.673(5)	1.661(4)	1.718(4)
H(2)–N–H(3)	107.63(21)		108.18(15)	
Hydrogen bonding				
O–O <sup>ii</sup>	2.636(3)	2.643(3)	2.656(3)	2.664(3)
H(1)–H(1 <sup>ii</sup> )	0.657(9)	0.712(8)	0.681(6)	0.718(6)
H(1)–O	0.992(5)	1.018(5)	0.992(3)	1.015(4)
H(1)...O <sup>ii</sup>	1.645(4)	1.662(4)	1.666(4)	1.680(4)
O–H(1)–H(1 <sup>ii</sup> )	172.56(1.37)		169.78(82)	
O–H(1)...O <sup>ii</sup>	177.04(54)		175.84(33)	
O...N <sup>i</sup>	2.852(1)	2.860(2)	2.851(2)	2.861(2)
O...H(3 <sup>i</sup> )	1.829(3)	1.853(3)	1.813(2)	1.838(2)
N–H(3)...O <sup>v</sup>	177.14(32)		176.66(20)	
O...H(2)	2.489(5)	2.516(5)	2.460(3)	2.489(3)

Symmetry code:

none:  $x, y, z$ ; (i):  $-y + 1/3, x - y - 1/3, z - 1/3$ ; (ii):  $-x + 2/3, -y + 1/3, -z + 1/3$ ;(iii):  $-y, x - y, z$ ; (iv):  $y, -x + y, -z$ ; (v):  $-x + y + 2/3, -x + 1/3, z + 1/3$ **Table M26-ii-003.** (NH<sub>4</sub>)<sub>2</sub>H<sub>3</sub>IO<sub>6</sub>. Quadrupole coupling constant  $e^2qQ/h$  and asymmetry parameter  $\eta$  of <sup>127</sup>I [70Kin].

<i>T</i>	$e^2qQ/h$ [MHz]	$\eta$	<sup>127</sup> I sites
RT (295...300 K)	25.35 (2)	0.00	All nuclei on 3-fold axis
94 K	93.2 (1)	0.00	<sup>1</sup> / <sub>4</sub> of all nuclei on 3-fold axis
	123 (1)	0.33	Two sets of <sup>3</sup> / <sub>8</sub> of all nuclei