

## The Crystal Structure of $N(C_2H_5)_4I_7$ at $-175^\circ C$

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The structure of  $N(C_2H_5)_4I_7$  (Havinga & Wiebenga, 1955) has been refined by means of three-dimensional Fourier syntheses. The reflection intensities were obtained from crystals at  $-175^\circ C$ . It is very likely that the  $I_3^-$  ions which occur in this compound are centrosymmetrical, in contradistinction to the  $I_3^-$  ions in  $CsI_3$  and some other polyiodides. The  $(F_\sigma-F_c)$  map indicates the positions of the light atoms.

### Introduction

In a preliminary report (Havinga & Wiebenga, 1955) the results were given of an X-ray study of  $N(C_2H_5)_4I_7$  at room temperature. There are four units  $N(C_2H_5)_4I_7$  in the orthorhombic unit cell; the probable space group is *Abam*. It was found that the structure consists of  $I_2$  molecules and  $I_3^-$  ions, which leave large holes for the  $N(C_2H_5)_4^+$  ions. The positions of the light atoms could be determined only approximately, by fitting a model of a  $N(C_2H_5)_4^+$  ion with the probable bond lengths and angles, on to  $(F_\sigma-F_c)$  syntheses of the three projections.

It appeared that with the assumption of a centrosymmetrical  $I_3^-$  ion in  $N(C_2H_5)_4I_7$ , as required by the symmetry of the space group *Abam*, a satisfactory agreement ( $R = 0.078$ ) between observed and calculated structure factors could be obtained. Centrosymmetrical or symmetrical  $I_3^-$  ions have also been reported for some triiodides with large cations (Mooney, 1938, 1943*a*, 1943*b* and 1957). In  $NH_4I_3$  (Mooney, 1935),  $CsI_3$  (Tasman & Boswijk, 1955) and  $CsI_4$  (Havinga, Boswijk & Wiebenga, 1954), however, the  $I_3^-$  ions are asymmetrical; in these three compounds, the two I-I bonds in the triiodide ion show, within the limits of error, the same difference in length of about  $0.2 \text{ \AA}$  and make the same angle of about  $176^\circ$ . The available data on the bond lengths and angles in the triiodide ion are summarized in Table 1.

Two alternative interpretations of these data may be suggested:

(1) The triiodide ion is essentially symmetrical with bond lengths of  $2.91 \text{ \AA}$ , which is the shape observed

in those cases (large cations) where the interaction between cations and anions is presumably small. In this interpretation deviations from the centrosymmetrical configuration are due to the interaction of the triiodide ion with its environment. It must be assumed that this interaction is approximately the same in  $NH_4I_3$ ,  $CsI_3$  and  $CsI_4$ . Since, in general, bond lengths do not change appreciably as a result of intermolecular interactions, it is remarkable that in the case of the polyiodides the changes should be so large. This might be due, however, to the fact that, judging from the large bond lengths, the bonds in these compounds are rather weak.

(2) The triiodide ion is essentially asymmetrical with bond lengths of  $2.84$  and  $3.02 \text{ \AA}$  and a bond angle of  $176.5^\circ$ , being the weighted average of the corresponding bond lengths and angles in  $NH_4I_3$ ,  $CsI_3$  and  $CsI_4$ . In this second interpretation it must be assumed that the symmetrical shape reported in the other compounds is not real, but is simulated by a statistical distribution of the asymmetrical triiodide ions over antiparallel orientations.

It would be possible to make a choice between the two interpretations, if the presence of a statistical distribution in those cases where symmetrical triiodide ions have been found, could be proved or disproved. This may be attempted by the use of the following arguments.

(a) In a Fourier synthesis the supposed average structure of asymmetrical triiodide ions shows a symmetrical arrangement of three electron-density peaks. The peaks, or some of them, may be somewhat more extended than the peaks due to atoms which are not

Table 1. Distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the triiodide ion  $I_b-I_a-I_b$  and their e.s.d.

	$I_b-I_a$	$I_a-I_b$	$I_b-I_b$	$I_b-I_a-I_b$
$NH_4I_3$	2.82	3.10	5.91	177
$CsI_3$	2.83 (0.015)	3.035 (0.015)	5.86 (0.016)	176.3 (0.5)
$CsI_4^*$	2.86 (0.012)	3.00 (0.012)	5.85 (0.018)	176.5 (0.5)
$As(C_2H_5)_4I_3$	2.90	2.90	5.80	176
$N(C_2H_5)_4I_7$ ( $20^\circ C$ .)*	2.91 (0.009)	2.91 (0.009)	5.81 (0.018)	180

\* The e.s.d. given for this compound are smaller than those in the original paper, because they are based on the results of a further refinement of the structure and a better determination of the cell dimensions.

subject to a statistical distribution over more than one position. It is to be expected, however, that the distance between the centres of gravity of the two outer peaks is equal to the distance between the outer atoms of the asymmetrical ion from which the symmetrical density distribution is composed. Therefore, a difference between the lengths of the symmetrical and asymmetrical ions would exclude the supposed average structure. Now, the length observed for the, seemingly or actually, symmetrical ions is  $5.81 \text{ \AA}$ , which is about  $0.05 \text{ \AA}$  less than the length of the asymmetrical ion. As this difference is only possibly significant, it does not give conclusive evidence against interpretation (2), although it makes it less likely.

(b) If the experimental accuracy were very high, it should be possible to detect whether or not an electron-density peak is a superposition of two (or more) atomic peaks, even when these are close together. In practice, an average structure of the type under discussion will merely present itself as a small extra thermal motion of one or more of the atoms of the triiodide ion. Strictly speaking, it will be impossible to distinguish the extra temperature factor from one due to a real extra thermal motion, except when the temperature is so low that the temperature factor due to thermal motion is small compared with the effect of the statistical distribution.

It was hoped that from a study of  $N(C_2H_5)_4I_7$  at  $-175^\circ C$ . by means of three-dimensional Fourier syntheses, more evidence could be obtained for the presence or absence of a statistical distribution of asymmetrical triiodide ions in this compound.

### Experimental

During the exposures a crystal was cooled by dripping liquid nitrogen on the glass capillary in which it was mounted on a glass hair. When the crystal was replaced by a thermocouple a temperature of  $-175^\circ C$ . was measured. The dimensions of the unit cell, which

Table 2. *Dimensions of the unit cell of  $N(C_2H_5)_4I_7$*

	20 °C.	-175 °C.
<i>a</i>	11.502 Å	11.236 Å
<i>b</i>	15.641	15.365
<i>c</i>	12.357	12.345
e.s.d. (%)	0.07	0.07

$$\lambda(Cu K\alpha_1) = 1.54051 \text{ \AA}, \quad \lambda(Cu K\alpha_2) = 1.54433 \text{ \AA}.$$

were deduced from photographs taken with a back-reflection camera, are given in Table 2.

The intensities of most reflections  $hkl$  at  $-175^\circ$  were estimated visually on oscillation photographs about the *c*-axis; some intensities were obtained from an oscillation photograph about the *b*-axis. The photographs were taken with Zr-filtered Mo-radiation, use was made of the multiple-film technique with three films of different speed behind each other. The oscillation range was  $13^\circ$ , the overlap for successive photographs  $3^\circ$ . The intensities of the reflections from different photographs were put on the same scale by comparing the intensities of reflections recorded two or more times. The relative intensities of about 1550 mutually independent reflections were obtained. As the crystals were small and regularly shaped ( $\mu R \approx 0.1$ ), no absorption correction was applied; errors due to oblique incidence were also neglected.

### Refinement of the structure

Starting from the final co-ordinates of the iodine atoms at room temperature, we obtained the co-ordinates of these atoms at low temperature from two successive [001] Fourier syntheses and one [010] Fourier synthesis; a correction for series termination errors was made.

With the new co-ordinates of the iodine atoms the structure factors  $hkl$  were calculated. Comparison with the experimental structure factors gave a temperature factor  $\exp(-B \sin^2 \theta/\lambda^2)$  with a *B* value of  $1.1 \text{ \AA}^2$ ; the disagreement index *R* was 0.15. The co-ordinates of the iodine atoms were more accurately determined by computing a three-dimensional Fourier synthesis. As is seen from Table 3 the co-ordinates remained practically the same, except for the *x* co-ordinate of atom  $I_b$  which changed a little. The three-dimensional Fourier synthesis indicated the positions of the light atoms.

The calculated structure factors  $hkl$  were now corrected for the change in the *x* co-ordinate of  $I_b$ , after which *R* amounted to 0.14; the contribution of the light atoms, which is very small, was not taken into account.\* Hereafter a three-dimensional ( $F_o - F_c$ ) synthesis was computed. The co-ordinates of the iodine

\* A list of observed and calculated structure factors  $hkl$  has been published (Havinga, 1957), and is available on request.

Table 3. *Co-ordinates of the iodine atoms after the different stages of refinement*

	$I_b$			$I_c$		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Projections at 20 °C.	0.9260	0.1777	0	0.1574	0.1932	0.1791
E.s.d.	0.0007	0.0005	—	0.0004	0.0003	0.0006
Projections at -175 °C.	0.9247	0.1800	0	0.1565	0.1945	0.1796
E.s.d.	0.0007	0.0005	—	0.0004	0.0003	0.0009
Three-dim. Fourier synth.	0.9234	0.1805	0	0.1562	0.1948	0.1796
Three-dim. ( $F_o - F_c$ ) synth.	0.9233	0.1805	0	0.1561	0.1947	0.1795
E.s.d. 0.0015 Å						

atoms, corrected with the help of this synthesis, were regarded as the final ones; they are listed in Table 3. The  $B$  values deduced from the three-dimensional ( $F_o-F_c$ ) synthesis are shown in Table 7 and discussed in the next section.

The indication of the positions of the light atoms in the three-dimensional Fourier synthesis was confirmed by the ( $F_o-F_c$ ) synthesis. There were maxima in a special, fourfold, position which had to be attributed to the four nitrogen atoms. In the space group  $Abam$ , to which the configuration of the iodine atoms seems to belong, the point symmetry of this fourfold position is  $2/m$ . Therefore the nitrogen atom of a tetrahedral  $N(C_2H_5)_4^+$  ion can only be put in the fourfold position if this ion is statistically distributed over two orientations, such that the resulting average distribution has the symmetry required. It appeared indeed that a model of the  $N(C_2H_5)_4^+$  ion could be fitted in two orientations on the more important maxima in the three-dimensional syntheses. The distances between these maxima corresponded to reasonable values for the bond lengths and angles. The co-ordinates of the carbon atoms, obtained in this way, are listed in Table 4.

Table 4. Co-ordinates of the light atoms at  $-175^\circ\text{C}$ .

	$x$	$y$	$z$
N	0	0	0.500
C <sub>1</sub>	0.100	0.047	0.442
C <sub>2</sub>	0.933	0.074	0.425
C <sub>3</sub>	0.858	0.050	0.328
C <sub>4</sub>	0.864	0.022	0.350

An alternative interpretation of the double number of carbon maxima may be given if it is assumed that the space group is  $Ab2$ ; which is, as well as  $Abam$ , in agreement with the systematic absences. In this space group there is no need for a statistical distribution of the  $N(C_2H_5)_4^+$  ions, since the point symmetry of the fourfold position is 2 instead of  $2/m$ . In this case the additional carbon peaks must be interpreted as ghosts due to the use of the phase angles  $0^\circ$  and  $180^\circ$  in the Fourier syntheses for the non-centric space group. The contribution of the light atoms to the structure factors is too small to make a decision between the alternative interpretations possible. The choice of the space group  $Abam$  is supported by the absence of a pyro- and piezo-electric effect and by the configuration of the iodine atoms, which is, as is shown in this paper, probably centrosymmetrical.

The heights of the peaks of the light atoms in the two three-dimensional syntheses are shown in Table 5a. As each carbon atom is distributed over two positions, the height of the carbon maxima is only

Table 5a. Peak heights of the I, N and C maxima in the three-dimensional syntheses ( $e.\text{\AA}^{-3}$ )

	I <sub>a</sub>	I <sub>b</sub>	I <sub>c</sub>	N	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>
$F_o$ synth.	314	301	315	10	7	7	7	8
( $F_o-F_c$ ) synth.	—	—	—	$5\frac{1}{2}$	5	6	6	7

about half the value one would expect for a carbon atom at  $-175^\circ\text{C}$ . The carbon peaks are hardly higher than the highest spurious peaks in the syntheses, which are listed in Table 5b. Since, however, the

Table 5b. Maximum values of spurious maxima and minima

	On special positions max.	min.	On general positions max.	min.
$F_o$ synth.	13	-11	6	-7
( $F_o-F_c$ ) synth.	9	-9	4	$-4\frac{1}{2}$

standard deviation in the electron-density at arbitrary positions is, according to the formula of Cruickshank (1949),  $2 e.\text{\AA}^{-3}$ , the carbon maxima in the ( $F_o-F_c$ ) synthesis are significant, whereas the highest spurious peaks are only possibly significant. The remarkably small peak height of the nitrogen maximum in the ( $F_o-F_c$ ) synthesis can only be explained by the large standard error for its special position.

### Discussion of the structure

The structure is shown in Fig. 1 and in two bounded projections, Fig. 2. The interatomic distances at

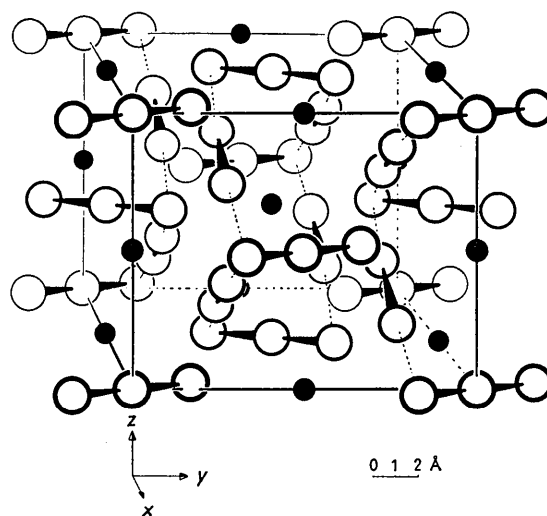


Fig. 1. The crystal structure of  $N(C_2H_5)_4I_7$ . The black spots indicate the centres of the positive ions.

Table 6. Distances between iodine atoms, with the e.s.d.

	$20^\circ\text{C}$ .	$-175^\circ\text{C}$ .
In the triiodide ion	2.91 (0.009)	2.904 (0.003)
In the iodine molecule	2.76 (0.013)	2.735 (0.003)
Other distances (see Fig. 2)	3.47 (0.011)	3.435 (0.003)
	4.43 (0.014)	4.432 (0.004)
	4.16 (0.007)	4.114 (0.004)
	4.55 (0.014)	4.486 (0.004)

$-175^\circ\text{C}$ . are given in Fig. 2, in Table 6 they are compared with the corresponding values at room temperature. The bond lengths and the second of the

other interatomic distances are not significantly different at the two temperatures.

In  $N(C_2H_5)_4I_7$  the atomic distance in the  $I_2$  molecules is only slightly larger than in crystalline iodine, where a bond length of 2.68 Å has been found (Kitaigorodskii, Khotsyanova & Struchkov, 1955). Neither is the shortest distance between iodine atoms of  $I_2$  molecules and  $I_3^-$  ions in  $N(C_2H_5)_4I_7$  much different from the shortest intermolecular distance in iodine crystals (3.56 Å). This indicates that the interaction between the  $I_2$  molecules and the  $I_3^-$  ions in  $N(C_2H_5)_4I_7$  is only little stronger than that between the  $I_2$  molecules in crystalline iodine, and that consequently this compound may be best described by the formula  $N(C_2H_5)_4I_3 \cdot 2 I_2$ .

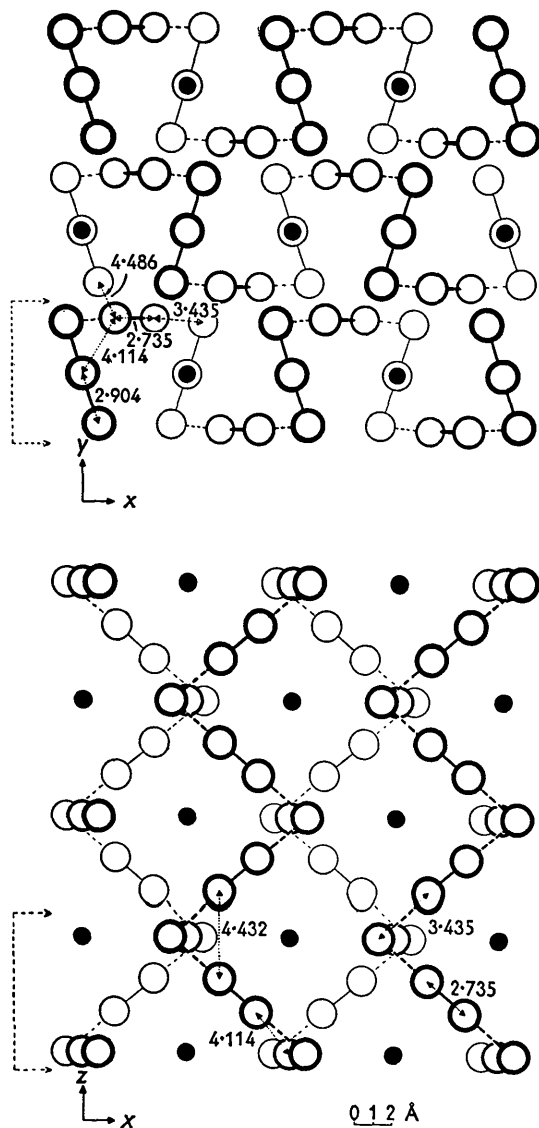


Fig. 2. Two bounded projections of the structure of  $N(C_2H_5)_4I_7$ . The part of the unit cell, projected in one figure, is indicated in the other figure.

#### The shape of the triiodide ion in $N(C_2H_5)_4I_7$

As was mentioned in the introduction, it was hoped that a study of the temperature factors of the iodine atoms in  $N(C_2H_5)_4I_7$  at  $-175^\circ C$ . would show whether or not the centrosymmetrical triiodide ion, as observed in this compound, is a result of a statistical distribution of asymmetrical  $I_3^-$  ions with bond lengths of 2.84 and 3.02 Å and a bond angle of  $176.5^\circ$ . It will be shown that the results obtained provide no indication in favour of an average structure and that, although an average structure cannot be excluded, the triiodide ions in  $N(C_2H_5)_4I_7$  are likely to be centrosymmetrical indeed.

The apparent extra temperature factors to be expected as a result of a statistical distribution depend on the kind of average structure assumed. It can be shown that a distribution of an atom over two positions lying  $2q$  Å apart will, to a first approximation, produce an extra  $B$  value of  $8\pi^2q^2$  Å<sup>2</sup> in the direction of the vector  $2q$ . If the asymmetrical triiodide ions are distributed over only two orientations, such that the terminal iodine atoms coincide in the two orientations, the central atom would be distributed over two positions lying  $2 \times 0.13$  Å apart; the result would be an extra, anisotropic, temperature factor for the central atom only, corresponding to an extra  $B$  value of  $8\pi^2(0.13)^2 = 1.3$  Å<sup>2</sup>. Other distributions are conceivable, however, in which the shifts are more or less equally divided between all three atoms of the triiodide ion and between the different directions in space. In this way it is even possible to imagine a statistical distribution over many positions lying close together, such that the three atoms of the resulting symmetrical averaged ion have equal extra, practically isotropic,  $B$  values of only  $8\pi^2(0.05)^2 = 0.2$  Å<sup>2</sup>. The  $B$  values actually observed for the atoms of the  $I_2$  molecules and  $I_3^-$  ions in  $N(C_2H_5)_4I_7$  are shown in Table 7. They were derived from the  $(F_o - F_c)$  synthesis by the application of a formula given by Hamilton (1955). The s.d. in the  $\bar{B}$  values was estimated to be 0.03 Å<sup>2</sup>, so that even differences of 0.2 Å<sup>2</sup> in  $\bar{B}$ , if present, could be detected.

Table 7 shows that the temperature factors are small

Table 7.  $B$  values (Å<sup>2</sup>) for the iodine atoms in  $N(C_2H_5)_4I_7$

	$B_x$	$B_y$	$B_z$	$\bar{B}$
$I_a$	1.05	0.96	1.10	1.04
$I_b$	1.04	0.83	1.13	1.00
$I_c$	1.05	0.93	1.09	1.02

$I_b - I_a - I_b$ , are triiodide ions,  $I_c - I_c$ , are iodine molecules.

and that those for the atoms of the triiodide ions are not significantly different from those for the atoms of the iodine molecules. This may be considered as evidence against an average structure. On the other hand, it can also be assumed that the real thermal motion of the atoms of the triiodide ions is smaller than that of the atoms of the iodine molecules, such

that the difference is just compensated by the effect of a statistical distribution. In that case one might expect that at room temperature the thermal motion of the atoms of the iodine molecules would be appreciably larger than that of the atoms of the triiodide ions. From  $(F_o - F_c)$  syntheses of the projections at room temperature it was shown, however, that the temperature factor of none of the iodine atoms differed significantly from the mean  $B$  value,  $5.2 \text{ \AA}^2$ , although the estimated standard deviation in the  $B$  values was not larger than about  $0.12 \text{ \AA}^2$ .

Therefore an average structure of  $N(C_2H_5)_4I_7$ , in which only the asymmetrical  $I_3^-$  ions are statistically distributed, does not seem to be very likely. The possibility of an average structure, involving equally the triiodide ions and the iodine molecules, possibly in connection with the two alternative orientations of the  $N(C_2H_5)_4^+$  ions, cannot be excluded.

A theoretical discussion of the bonds in polyhalogen compounds by the LCAO method has been given elsewhere (Havinga, 1957). It was shown that centrosymmetrical triiodide ions may be expected and that the deviation from centrosymmetry in compounds like  $CsI_3$  may be explained by the interaction of the cations and anions.

Our thanks are due to Dr Aafje Vos for many improvements of the manuscript. The Fourier syntheses

were calculated on punched-card machines. We wish to express our gratitude to Theodorus Niemeijer N.V. for generously putting their I.B.M. equipment at our disposal and to Mr M. R. van der Velde and Miss G. E. Veldman for their assistance in operating these machines. We also thank Mr H. Schürer for his assistance in many of the calculations. The Netherlands Organisation for Pure Research (Z. W. O.) supported this work indirectly.

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## Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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**The crystal structures of  $ThHg_3$ ,  $ThIn_3$ ,  $ThTl_3$ ,  $ThSn_3$  and  $ThPb_3$ .** By RICCARDO FERRO, *Chemical Institute, Laboratory of Physical Chemistry of Genoa University, Genoa, Italy*

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### The compound $ThHg_3$

The compound  $ThHg_3$  has been prepared and studied by Baenziger, Rundle & Snow (1956). They found that it is closed-packed hexagonal with  $a_1 = 3.38$  and  $a_3 = 4.72 \text{ \AA}$ , and they do not exclude the possibility of solid-solution formation. The present author has found the same structure but has obtained slightly different values for the unit-cell edges; he has not succeeded in observing the formation of solid solutions. Several samples containing a variable mercury content around that of  $ThHg_3$  (Th% theor. = 27.83) have been prepared. Two samples, which when analyzed were found to have a Th content of 27.3 and 28.5% respectively, have shown Debye lines which are characteristic of the  $ThHg_3$  phase. The same reflexions with the same values for the lattice parameters have also been observed (both alone and mixed with the

lines of other phases) in other samples containing quantities of Th a little higher or a little lower.

The constants (obtained by the Straumanis powder method, with  $Cu K\alpha_1$  radiation  $\lambda = 1.540500 \text{ \AA}$ ) are in Table I together with those of the isostructural  $LaHg_3$  (Iandelli & Ferro, 1951) and  $UHg_3$  (Rundle & Wilson, 1949):

Table I. *Lattice constants ( $\text{\AA}$ ) and densities ( $\text{g.cm.}^{-3}$ ) for isostructural compounds  $MeHg_3$*

	$LaHg_3$	$ThHg_3$	$UHg_3$
$a_1$	3.411	3.364	3.327
$a_3$	4.961	4.907	4.888
$a_3/a_1$	1.454	1.459	1.469
$\rho_x$	12.30	14.39	14.88

As we can observe, all the axial ratios are very similar.