Acta Cryst. (1954). **7**, 277

The Crystal Structures of $NaHg_2$, NaHg and Na_3Hg_2

By J. W. Nielsen and N. C. Baenziger

Department of Chemistry, The State University of Iowa, Iowa City, Iowa, U.S.A.

(*Received* 10 *August* 1953)

The crystal structures of NaHg and Na_3Hg_2 have been determined from Weissenberg and precession camera data. NaHg is end-centered orthorhombic, $a = 7{\cdot}19$, $b = 10{\cdot}79$, $c = 5{\cdot}21$ Å, $Z = 8$. Pairs of mercury atoms are grouped in ribbons which extend through the crystal. Na_3Hg_2 is tetragonal with $a = 8{\cdot}52$, $c = 7{\cdot}80$ Å, $Z = 4$. Mercury atoms are in isolated groups of four with a nearly square arrangement. From powder diagrams $NaHg_2$ was found to be the hexagonal AlB_2 type with $a = 5{\cdot}029$, $c = 3{\cdot}230$ Å.

Introduction

The determination of the crystal structures of the sodium amalgams has been undertaken as part of a program for determining the structures of compounds formed by the alkali, alkaline earth and similar metals with the metals of group II-B. Of the five sodium–mercury compounds which are reported here, $NaHg_4$, $NaHg_2$, NaHg, Na_3Hg_2 and Na_5Hg_2, the structures of three, $NaHg_2$, NaHg and Na_3Hg_2, have been completed. There is considerable disagreement in the older literature as to the number and composition of the sodium amalgams (Hansen, 1936), and further work is necessary to determine the number, composition and structure of the remaining sodium–mercury compounds.

Experimental technique

Since the compounds of sodium and mercury decompose rapidly in the presence of oxygen or moisture, it is necessary to carry out all the preparations in an inert atmosphere or under vacuum. The procedure for preparing the amalgams was to bring known amounts of pure mercury and pure sodium together in a reaction vessel through which dry nitrogen was flowing at a rapid rate. Since the reaction is quite exothermic, the mixing was done slowly and a homogeneous sample was obtained by merely shaking the reaction vessel. Subsequent analyses indicated that the samples were homogeneous and that the compositions were those desired to within 1% of the molar ratio.

Although this technique produced excellent powder specimens, it was found necessary to modify the method slightly to obtain single crystals. By preparing a sample having the desired atomic ratio and then altering its compositions slightly by adding a small amount of sodium or mercury, so that the crystals could form from the melt over a range of temperatures, it was possible to obtain single-crystal specimens. The adjustment of composition was done by trial and error. The sample was melted under vacuum in a small vessel fitted with a closed side-arm tube into which the pure molten alloy was poured and allowed to cool. This side-arm tube was then sealed off under vacuum.

Single crystals were mounted in capillaries by breaking the sample tubes under an inert atmosphere, scraping some crystals free from the sample, and picking up these crystals with a capillary previously coated inside with Canada balsam and attached to an aspirator. This capillary was sealed and examined under a microscope for single crystals, likely specimens were selected, and the capillary was sealed off on each side of the crystals at a convenient distance. The crystal was fixed in place by gently warming the capillary until the Canada balsam softened. Since this method often resulted in chips of crystals, the Buerger precession camera was very useful in aligning the specimens. Commercial nitrogen which had been passed through a drying train was used as an inert atmosphere. Single crystal specimens mounted in the manner outlined have kept for nine months without signs of decomposition.

$NaHg_2$

$NaHg_2$ was found from a powder diagram to be isostructural with the aluminum boride type. The hexagonal cell has the dimensions

$$a = 5{\cdot}0290 \pm 5,\ c = 3{\cdot}2304 \pm 16\ \text{Å},\ U = 70{\cdot}9\ \text{Å}^3,$$
$$Z = 1,\ D_x = 9{\cdot}96\ \text{g.cm.}^{-3}.$$

The density from the data of Maey (1899) is 9·94 g.cm.^{-3}.

Unlike those of the other sodium amalgams, the lines in the back-reflection region for $NaHg_2$ (m.p. 349° C.) were sufficiently resolved to obtain a precise determination of the lattice constants by the method of Cohen (1935). The precision measure was calculated by the method of Jette & Foote (1935). The interatomic distances are given in Table 1.

Table 1. *Interatomic distances in* $NaHg_2$

Atom	Number of neighbors	Distance (Å)
Na	12 Hg	3·16
	2 Na	3·23
Hg	3 Hg	2·90
	6 Na	3·16
	2 Hg	3·23

NaHg

NaHg is gold in color, which strikingly differentiates it from the other sodium amalgams observed. Zero-layer Weissenberg data (*hk*0) were obtained from a single crystal with Cu $K\alpha$ and Mo $K\alpha$ radiation. The Buerger precession camera using Mo $K\alpha$ radiation ($\mu = 25°$, magnification factor, 6·00) was employed to obtain (*h*0*l*) and (0*kl*) data. Intensities were estimated visually, using a graduated scale. Crude absorption corrections were made assuming a cylindrical rod shape for the crystal for the Weissenberg data, and a flat plate shape for the precession data. The end-centered orthorhombic unit cell dimensions as determined from a powder diagram are

$$a = 7{\cdot}19,\ b = 10{\cdot}79,\ c = 5{\cdot}21\ \text{Å},\ U = 404\ \text{Å}^3,$$
$$Z = 8,\ D_x = 7{\cdot}36\ \text{g.cm.}^{-3}.$$

The density reported by Maey (1899) is 7·26 g.cm.$^{-3}$.

The reflections observed were those characteristic for the space groups $Cmc\text{–}C_{2v}^{12}$, $C2cm\text{–}C_{2v}^{16}$ or $Cmcm\text{–}D_{2h}^{17}$. Since *C*2*cm* places two atoms directly over one another in the *c* direction and *c* is only 5·21 Å, this space group was not considered. *Cmcm* was assumed to be the correct space group in preliminary work. *Cmc*, which contains an additional parameter, was not needed to secure intensity agreement.

A Patterson projection made using (*hk*0) data was interpreted to give a rough picture of the structure. The structure was further refined by electron-density projections on (100) and (001) followed by least-squares treatment of the combined (*hk*0), (0*kl*) and (*h*0*l*) data. The electron-density maps (Figs. 1 and 2) did not give a clear indication of sodium atom positions (nor did $F_o - F_c$ maps), so positions were assumed prior to the least-squares treatment which would place them as nearly equidistant from their neighbors as possible. The least-squares treatment produced a shift from these values ($y_{\text{Na}} = 0{\cdot}36$ and $0{\cdot}82$) to the values listed below. A negligible shift (−0·0003 parameter units) was found for the mercury atoms.

Table 2. *Structure-factor data for* NaHg

Indices	F_o	F_c
200	414	−419
400	255	284
600	—	7
800	57	−40
10,0,0	57	76
110	*	—
310	220	−271
510	228	254
710	129	−183
910	63	87
020	250	231
220	189	−229
420	93	81
620	—	−27
820	—	−30
10,2,0	—	27
130	—	−15
330	—	20
530	—	−27
730	—	16
930	—	8
040	276	−309
240	220	197
440	145	−133
640	—	6
840	—	21
10,4,0	—	−38
150	102	−52
350	219	234
550	226	−195
750	159	164
950	80	−71
060	356	−326
260	252	304
460	145	−132
660	—	34
860	—	43
10,6,0	39	−46
170	115	−73
370	130	107
570	161	−145
770	102	89
970	59	−53
080	105	−73
280	88	59
480	—	−32
680	—	5
880	—	8
190	—	4
390	—	−38
590	—	28
790	—	−28
990	—	11
0,10,0	146	124
2,10,0	102	−106
4,10,0	57	55
6,10,0	—	−11
1,11,0	64	44
3,11,0	90	−68
5,11,0	103	93
7,11,0	79	−59
9,11,0	39	35
0,12,0	110	102
2,12,0	102	−91
4,12,0	46	35
1,13,0	—	6
3,13,0	—	−33
002	314	−516
004	232	266
006	105	−109
202	282	318
204	178	−176
206	51	76
402	211	−221
404	64	123
602	—	7
604	—	6
802	47	34
021	331	−419
022	170	−173
023	257	257
024	128	94
025	125	−126
026	58	−40
041	369	−383
042	251	242
043	257	244
044	140	−132
045	131	−117
061	74	52
062	360	258
063	65	−36
064	143	−152
065	—	18
081	252	237
082	71	61
083	163	−165
084	49	−36
0,10,1	114	114
0,10,2	108	−104
0,10,3	92	−81
0,12,1	34	−43
0,12,2	84	−86

* Not estimated because of background.

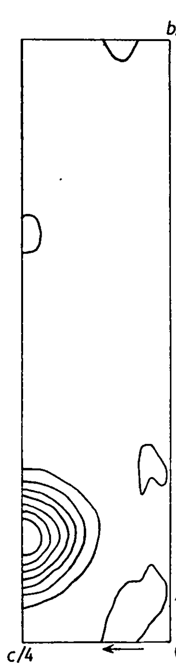

Fig. 1.

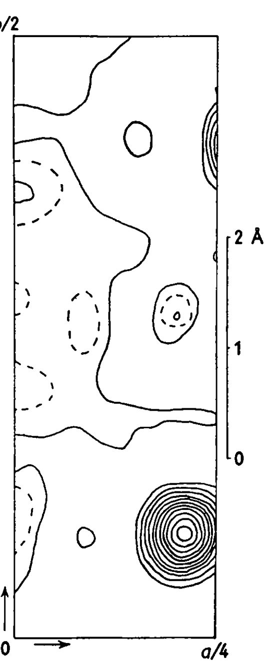

Fig. 2.

Fig. 1. Electron density of NaHg projected on (100).
Fig. 2. Electron density of NaHg projected on (001).

$$(0, 0, 0),\ (\tfrac{1}{2}, \tfrac{1}{2}, 0)+$$

8 Hg in (g): $x, y, \frac{1}{4};\ \bar{x}, y, \frac{1}{4};\ x, \bar{y}, \frac{3}{4};\ \bar{x}, \bar{y}, \frac{3}{4}$
with $x = 0{\cdot}212\pm0{\cdot}001_5$, $y = 0{\cdot}088\pm0{\cdot}001_0$.

4 Na_1 in (c): $0, y, \frac{3}{4};\ 0, \bar{y}, \frac{3}{4}$, with $y = 0{\cdot}368\pm0{\cdot}010$.
4 Na_2 in (c): with $y = 0{\cdot}814\pm0{\cdot}006$.

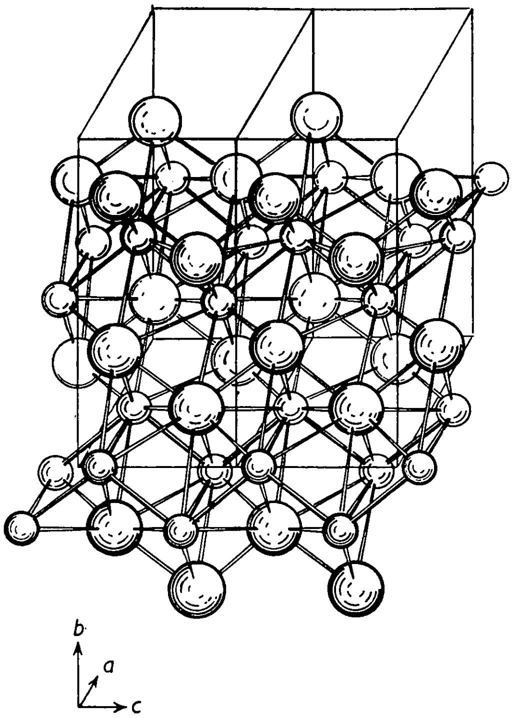

Fig. 3. Structure of NaHg. Large atoms are Na. Two unit cells are shown with some of the atoms repeated by the unit translations in the *a* and *b* directions omitted.

The standard deviations in the parameters which are listed above were determined from the least-squares treatment (Cruickshank, 1949*a*). The value of $R = \Sigma||F_o|-|F_c||\div\Sigma F_o$ prior to the least-squares treatment was 0·207 if all reflections were included, 0·150 if F's were omitted when F_o was zero. After the least-squares refinement, the values of R were 0·203 and 0·146 respectively, indicating the relative insensitivity of the discrepancy factor to the positions of the sodium atoms. The temperature factor used to adjust the calculated to the observed data had a value of $B = 3{\cdot}55$ Å^2. The structure-factor data are listed in Table 2. The final structure is shown in Fig. 3. A list of interatomic distances is given in Table 3.

Table 3. *Interatomic distances in* NaHg

Atom	Number of neighbors	Distance (Å)
Hg	1 Hg	3·05
	2 Hg	3·22
	1 Na_1	3·14
	3 Na_2	3·20
	1 Na_2	3·33
	2 Na_1	3·36
	1 Na_1	3·38
Na_1	2 Hg	3·14
	2 Na_2	3·26
	4 Hg	3·36
	2 Hg	3·38
	2 Na_2	3·64
Na_2	6 Hg	3·20
	2 Na_1	3·26
	2 Hg	3·33
	2 Na_1	3·64

Na_3Hg_2

Na_3Hg_2 has a primitive tetragonal unit cell with $a = 8{\cdot}52$, $c = 7{\cdot}80$ Å, $U = 566$ Å^3, D_m (Maey, 1899) $= 5{\cdot}55$ g.cm.$^{-3}$, $Z = 4$, $D_x = 5{\cdot}51$ g.cm.$^{-3}$, formula weight = 470·21.

The general extinctions which were observed, $(0kl)$ present only with $k+l$ even, are those which are characteristic for space groups $P4_2/mnm$, $P4n2$ and $P4_2nm$. Precession camera diagrams were used to obtain $(hk0)$ data (Mo $K\alpha$ radiation) and Weissenberg diagrams were made to obtain the $(0kl)$ data (Cu $K\alpha$) from the same crystal. Intensities were estimated visually as for NaHg.

Preliminary positions for the mercury atoms were obtained by inspection of the $(hk0)$ precession diagrams. The electron-density projection made using the $F(hk0)$ data clearly indicated the positions of the mercury atoms as well as the positions of four of the twelve sodium atoms. Additional small peaks were also present in the electron-density map but in twice as great a number as sodium atoms in the structure. The eightfold set of peaks labeled A in Fig. 4 could be eliminated on spatial considerations. Satisfactory distances between atoms could be obtained by placing the atoms at the other peaks on the electron-density map.

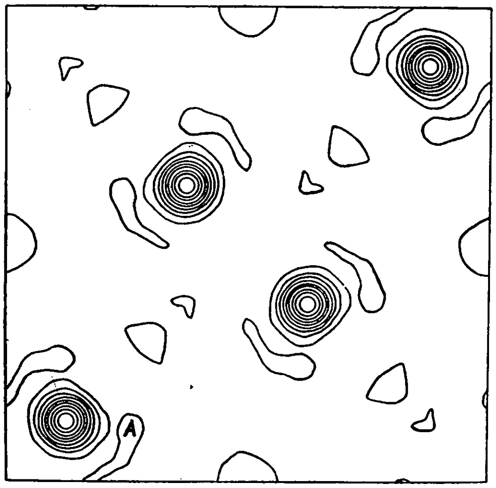

Fig. 4. Electron density of Na_3Hg_2 projected on (001).

A least-squares refinement of the data indicated a negligible shift for the mercury atom, 0·005 parameter unit for one type of sodium atom and 0·001 parameter unit for the other.

The atomic positions are

8 Hg in (j): $x, x, z;\ \bar{x}, \bar{x}, z;\ \frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}+z;$
$\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}+z;\ x, x, \bar{z};\ \bar{x}, \bar{x}, \bar{x};$
$\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}-z;\ \frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}-z$
with $x+0{\cdot}125\pm0{\cdot}0005,\ z = 0{\cdot}190\pm0{\cdot}001.$

4 Na_1 in (g): $x, \bar{x}, 0;\ \bar{x}, x, 0;\ \frac{1}{2}+x, \frac{1}{2}+x, \frac{1}{2};$
$\frac{1}{2}-x, \frac{1}{2}-x, \frac{1}{2}$
with $x = 0{\cdot}210\pm0{\cdot}010.$

4 Na_2 in (f): $x, x, 0;\ \bar{x}, \bar{x}, 0;\ \frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2};$
$\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}$
with $x = 0{\cdot}368\pm0{\cdot}010.$

4 Na_3 in (c): $0, \frac{1}{2}, 0;\ \frac{1}{2}, 0, 0;\ 0, \frac{1}{2}, \frac{1}{2};\ \frac{1}{2}. 0, \frac{1}{2}.$

The errors in the atomic parameters are standard deviations as calculated from the least-squares treatment. The standard deviation of the x, y coordinates of the sodium atom in special position (c) is 0·04 Å, as determined from the electron-density maps by Cruickshank's method (Cruickshank, 1949*b*). The discrepancy factor, R, for the $(hk0)$ data is 0·084.

The z parameters were obtained from examination of the $(0kl)$ data. If the structure is assumed to be based on space group $P4_2/mnm$, then spatial considerations fix the positions of the Na_1 and Na_2 atoms; there is a choice in the positions of the Na_3 atoms to be located in (c) with z values of 0 and $\frac{1}{2}$, or in (d) with z values of $\frac{1}{4}$ and $\frac{3}{4}$; and the z parameter of the mercury atoms must be determined. A Patterson projection using $F^2(0kl)$ data clearly showed that the Hg atoms were separated by about $\frac{3}{8}c$ in the [001] direction, and it indicated that the Na_3 atoms were in position (c). Structure factors calculated with $z_{Hg} = 0{\cdot}190$ gave good agreement with the observed values.

Table 4. *Structure-factor data for* Na_3Hg_2

Indices	F_o	F_c
200	—	1
400	373	−391
600	—	18
800	180	179
10,0,0	15	5
110	267	277
210	353	−337
310	296	−283
410	36	−23
510	195	−185
610	199	192
710	111	99
810	—	−5
910	58	60
10,1,0	66	−62
220	44	56
320	298	−300
420	36	14
520	209	206
620	19	14
720	151	138
820	—	9
920	84	−82
330	195	196
430	59	10
530	129	121
630	150	14
730	96	102
830	—	6
930	71	−64
440	292	330
540	—	0
640	—	7
740	—	−1
840	135	−131
940	—	2
550	97	108
650	116	−115
750	97	−87
850	—	−3
660	19	7
760	86	−82
860	—	5
770	49	52
002	300	−280
004	101	91
006	175	170
008	133	129
011	212	137
013	297	298
015	210	181
017	84	50
019	18	18
020	0	1
022	—	2
024	—	2
026	—	−17
028	—	1
031	151	−118
033	218	235
035	176	−155
037	70	46
040	323	387
042	204	268
044	—	−8
046	149	105
048	163	108
051	55	49
053	160	181
055	124	127
057	65	44
060	—	−13
062	—	8
064	—	7
066	—	4
071	25	32
073	93	110
075	73	69
077	44	28
080	138	154
082	86	−88
084	14	13
086	60	51
091	—	35
093	49	59
095	60	48

A least-squares treatment of only the mercury parameter indicated no change in the Hg positions. No attempt was made to vary the (x, y) coordinates of the atoms since these were fixed adequately by the $F(hk0)$ data. The $F(hk0)$ data were freer from absorption effects than the $F(0kl)$ data and therefore were judged to be more reliable.

Placing the sodium atoms in positions (*c*) seemed to create unnecessarily short distances between sodium atoms. These distances could be made longer by placing the atoms in positions (*d*). This change in the sodium positions increased the R value from 0·20 to 0·23, indicating that the sodium atoms were correctly placed in positions (*c*).

In obtaining the best fit of calculated to observed F values, slightly different temperature factors were found for the $(hk0)$ and $(0kl)$ data ($B = 3{\cdot}55$ Å^2 for $(hk0)$ data, 4·57 Å^2 for $(0kl)$). This difference can be ascribed to a partial correction for absorption effects which differed in the two sets of data.

An examination of the other space-group possibilities shows that, with fixed x and y coordinates, no different z arrangements are possible for the mercury atoms. The positions of the Na_3 atoms can be altered along the c axis by arbitrary amounts, but the intensity data do not support such changes. The combined R value for $(hk0)$ and $(0kl)$ data for the structure given above is 0·125. The calculated and observed F values are listed in Table 4. Interatomic distances are listed in Table 5. In the diagram of the structure given in Fig. 5, some of the atoms on the front and rear faces of the cell have been omitted for greater clarity.

Table 5. *Interatomic distances in* Na_3Hg_2

Atom	Number of neighbors	Distance (Å)
Hg	1 Hg	2·96
	1 Hg	3·01
	1 Na_1	3·13
	2 Na_2	3·26
	1 Na_2	3·28
	2 Na_1	3·30
	2 Na_3	3·68
Na_1	2 Na_3	3·05
	2 Hg	3·13
	4 Hg	3·30
Na_2	1 Na_2	3·18
	4 Hg	3·26
	2 Hg	3·28
	2 Na_3	3·33
Na_3	2 Na_1	3·05
	2 Na_2	3·33
	4 Hg	3·68

Other Na–Hg phases

Preliminary data have been obtained by Weissenberg methods of $NaHg_4$ and by precession camera methods of a phase tentatively designated as Na_5Hg_2. $NaHg_4$ has a hexagonal unit cell with $a = 61{\cdot}5$, $c = 9{\cdot}7$ Å. The cell could contain about 230 units of $NaHg_4$. Na_5Hg_2 is rhombohedral with $a = 18{\cdot}52$ Å, $\alpha = 29° 23'$ (hexagonal cell dimensions, $a = 9{\cdot}39$, $c = 53{\cdot}1$ Å).

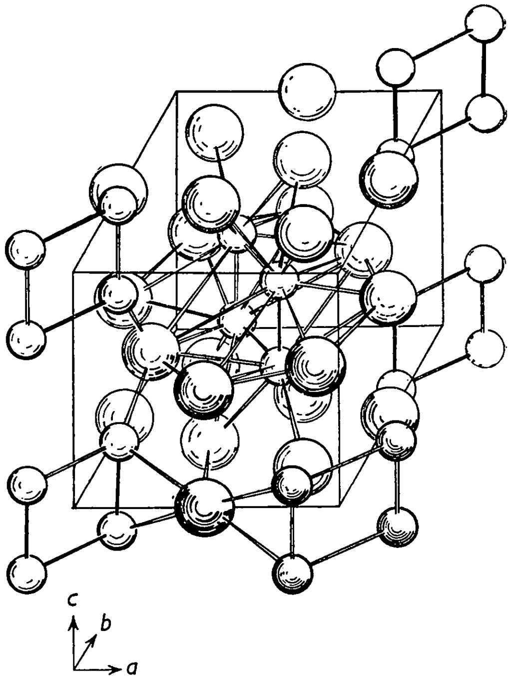

Fig. 5. Structure of Na_3Hg_2. Small atoms are Hg. Some of the atoms repeated by the unit translations have been omitted for greater clarity.

Discussion of the structures

$NaHg_2$ is isostructural with UHg_2 (Rundle & Wilson, 1949) and has very nearly the same unit cell dimensions (UHg_2, $a = 4{\cdot}99$, $c = 3{\cdot}23$ Å; $NaHg_2$, $a = 5{\cdot}029$, $c = 3{\cdot}23$ Å). The distances between the atoms in this structure are considerably shorter than in the elements, corresponding to the marked decrease in volume upon formation from the elements of 18·9% and the high exothermicity of the formation reaction.

The nature of the environment of the Hg atoms in this structure is such that if, according to Pauling (1947, 1949), one assumes a valence and a corresponding single-bond radius for Hg, then, in order to obtain a self-consistent calculated valence for Hg, the single-bond radius and valence of sodium are no longer arbitrary. Table 6 shows a listing of assumed valences

Table 6. *Calculation of* Na *valence in* $NaHg_2$

Assumed valence of Hg	R_1 for Hg*	Calculated R_1 for Na	Calculated valence for Na
6	1·348	1·729	12·1
4·5	1·391	1·512	5·4
4	1·406	1·386	3·3
3·5	1·421	1·142	1·3

* Pauling's radii have been converted to Å from kX. units.

for Hg and the corresponding valences and single-bond radii for Na. The most reasonable values according to this scheme would appear to be Hg with a valence of about 4 and Na with a valence of about 3.

In the NaHg structure the mercury atoms group themselves in pairs at a distance close to that in mercury metal, Hg–Hg = 3·05 Å. The pairs are further grouped into ribbons in which the Hg–Hg distance is 3·22 Å between Hg_2 pairs in the ribbon. These zigzag ribbons extend in the [001] direction in the unit cell and form a *C* end-centered arrangement. The sodium atoms zigzag along [001] between these ribbons.

The Na_3Hg_2 structure has Hg_4 groups which are nearly square in arrangement. The Hg_4 group could be considered as two Hg_2 groups which are rather tightly bound. The Hg_4 units are isolated in the structure, being completely surrounded by sodium atoms. The Hg–Hg distances in the Hg_4 groups, 3·01 and 2·96 Å, are again very close to the values in mercury metal.

The sodium–mercury structures fall into a pattern indicated by Zn and Cd (*B*-type atoms) with more electropositive elements such as the alkali, alkaline earth and rare earth metals (*A*-type atoms). When the ratio of *B* to *A* atoms is high, the *B* lattice is three-dimensional in character and determines the size of the unit cell and also the size of the holes in the lattice in which the other element is placed. The hole will accommodate the more compressible *A* elements over a considerable range of sizes less than the size of the hole, but not greater than this size. This is the case for the $NaZn_{13}$-type structure (*Strukturbericht*, 1941), the $BaCd_{11}$-type (Sanderson & Baenziger, 1953) and the $CaZn_5$-type (*Structure Reports*, 1951). When the ratio of *B* to *A* diminishes, the three-dimensional framework of *B* atoms must necessarily disappear, but the *B*-type atoms tend to remain grouped together as long as possible. In NaHg, *B* atoms group into ribbons; in Na_3Hg_2 the *B* atoms are in isolated groups of four. Preliminary structural investigation of Na_5Hg_2 indicates that the Hg atoms are isolated in the structure. $NaHg_2$ might be considered as transitional between a three-dimensional net of Hg atoms and a two-dimensional layer net of Hg atoms.

Further data on the structures of *A*-type elements with the *B*-type elements are very meagre, so that the extent of the structural sequence is unknown. However, a sodium–lead structure, NaPb, contains tetrahedral Pb_4 units isolated in the structure (Marsh & Shoemaker, 1953).

This work was done under contract AT(11-1)-72, Project No. 4, with the U.S. Atomic Energy Commission. One of us (J. W. N.) wishes to acknowledge support from an Allied Chemical and Dye Corporation fellowship for part of this work.

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