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# Redetermination of $Na_3Hg_2$

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The sodium amalgam trisodium dimercuride, $Na_3Hg_2$, adopts a unique structure type, containing isolated square $Hg_4$ clusters as found previously [Nielsen & Baenziger (1954). *Acta Cryst.* **7**, 277–282]. However, redetermination of the structure supported the placement of one of the Na atoms in a different site, leading to more reasonable Na···Na distances.

**Key indicators**

Single-crystal X-ray study
$T$ = 193 K
Mean $\sigma$(Hg–Hg) = 0.001 Å
$R$ factor = 0.038
$wR$ factor = 0.102
Data-to-parameter ratio = 33.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

## Comment

The structures of alkali metal amalgams are still not completely characterized, despite their long history (Deiseroth, 1997). In the Na—Hg system, the phases $NaHg_4$, $NaHg_2$, NaHg ($\alpha$,$\beta$,$\gamma$), $Na_3Hg_2$, $Na_8Hg_3$ ($\alpha$,$\beta$,$\gamma$) and $Na_3Hg$ ($\alpha$,$\beta$) have now been identified, with the structure of only $NaHg_4$ remaining unsolved (Deiseroth *et al.*, 1997). [The existence of two modifications of $Na_7Hg_8$ is uncertain (Kober & Nichkov, 1975).] The tetragonal structure of $Na_3Hg_2$ (Pearson symbol *tP*20, space group $P4_2/mnm$) was determined previously from photographic data (Nielsen & Baenziger, 1954). The data examined were limited to *hk*0 (precession) and 0*kl* reflections (Weissenberg), leading to a high residual factor of $R$ = 0.125. Moreover, anomalously short Na···Na distances (3.05 Å) were noted in the structural model in which one of the Na atoms is located in Wyckoff site 4*c* (0, $\frac{1}{2}$, 0). An alternative model in which this Na atom is placed in 4*d* (0, $\frac{1}{2}$, $\frac{1}{4}$) was considered but was rejected owing to an apparent lack of improvement in the refinement.

Redetermination of the structure of $Na_3Hg_2$ from diffractometer data confirms that the proposed alternative model was

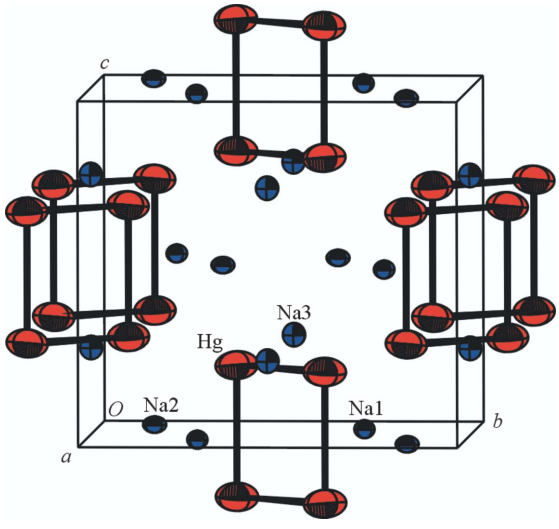


**Figure 1**
Projection of $Na_3Hg_2$ approximately along the *a* axis. Displacement ellipsoids are drawn at the 50% probability level.

correct after all. Fig. 1 shows that the structure consists of nearly square $Hg_4$ clusters that are separated by Na atoms. Although the most important correction is in the position of the Na3 site (located on the $z = \frac{1}{4}$ and $\frac{3}{4}$ planes instead of the $z$ = 0 and $\frac{1}{2}$ planes), there are also minor shifts in the Na1 and Na2 sites (by 0.05–0.10 Å). The coordination of Hg atoms remains roughly trigonal prismatic around Na1 and Na2. In the previous structure model, the coordination of Hg atoms around Na3 was square planar, at rather long distances (3.68 Å); in the present structure model, the coordination is flattened tetrahedral, at more reasonable distances [3.3756 (4) Å]. The shortest Na···Na distance [3.395 (8) Å] is now similar to those in other Na—Hg phases, but it is still significantly shorter than that in elemental Na (3.72 Å; Donohue, 1974), a reflection of the molar volume reduction and partial ionic character generally found in all alkali metal amalgams (Deiseroth, 1997).

## Experimental

Air- and moisture-sensitive crystals of $Na_3Hg_2$ were obtained in an attempt to prepare $NaHg_4$ by reaction of a 0.3 g stoichiometric mixture of the elements (99.9% or greater purity) placed in an arc-welded Ta container under argon and then sealed within a fused-silica tube under vacuum. The mixture was heated at 1173 K for 2 d and then slowly cooled to room temperature over a period of 5 d. A selected prismatic crystal was mounted under paraffin oil in a thin-walled glass capillary. Other binary Na–Hg phases were presumed to be formed in the reaction, but the air sensitivity of the sample prevented complete characterization.

*Crystal data*

$Na_3Hg_2$
$M_r$ = 470.15
Tetragonal, $P4_2/mnm$
$a$ = 8.4587 (5) Å
$c$ = 7.7078 (4) Å
$V$ = 551.49 (5) Å$^3$
$Z$ = 4
$D_x$ = 5.662 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu$ = 55.67 mm$^{-1}$
$T$ = 193 (2) K
Prism, gold
0.41 × 0.18 × 0.08 mm

*Data collection*

Bruker Platform/SMART 1000 CCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 2001)
$T_{min}$ = 0.003, $T_{max}$ = 0.069
7237 measured reflections
600 independent reflections
410 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.088
$\theta_{max}$ = 33.1°

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.102
$S$ = 1.16
600 reflections
18 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 5.3809P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 3.16 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.89 e Å$^{-3}$
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0063 (6)

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Hg—Hg$^{i}$ | 2.9352 (10) | Na2—Hg$^{i}$ | 3.153 (8) |
| Hg—Hg$^{ii}$ | 2.9878 (11) | Na2—Hg$^{v}$ | 3.287 (5) |
| Na1—Hg$^{iii}$ | 3.128 (5) | Na2—Na2$^{vi}$ | 3.395 (8) |
| Na1—Hg$^{i}$ | 3.234 (6) | Na2···Na3 | 3.786 (3) |
| Na1···Na3 | 3.596 (5) | Na3—Hg$^{iii}$ | 3.3756 (4) |
| Na1···Na2$^{iv}$ | 3.905 (8) | | |

Symmetry codes: (i) $x, y, -z$; (ii) $-x+1, -y+1, z$; (iii) $-y+\frac{1}{2}, x+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x, y+1, z$; (v) $y-\frac{1}{2}, -x+\frac{1}{2}, z-\frac{1}{2}$; (vi) $-x, -y, -z$.

Compared with the previous refinement (Nielsen & Baenziger, 1954), the present refinement is characterized by improved reliability factors (from 0.125 to 0.038), decreased s.u. in interatomic distances (from >0.01 Å to 0.005 Å) and the description of displacement parameters for individual atoms instead of a global value for all data. The maximum peak and deepest hole are located 0.83 Å and 0.76 Å, respectively, from Hg and Na1.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXTL*.

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