

Polymorphism of NaHg: The First Experimental Observation of a Reversible, Temperature Driven B2 (CsCl) – B32 (NaTl) Phase Transition

Matthias Rochnia and Hans-Jörg Deiseroth

Anorganische Chemie II, Fb8, Universität-GH Siegen, D-57068 Siegen

Received November 18, 1994; accepted December 10, 1994

Based on combined X-ray analyses and thermal investigations, the intermetallic compound NaHg is shown to exist in three different modifications (α -, β - and γ -NaHg). The already known low temperature modification α -NaHg is an orthorhombically distorted variant of the CsCl (B2) structure. At 165 °C, α -NaHg transforms in a reconstructive first order transition of β -NaHg, a slightly rhombohedrally distorted variant of the NaTl (B32) type ($a = 5.071(8)$, $c = 12.668(31)$ Å, space group $R3m$). In a subsequent displacive first order transition at 176 °C, γ -NaHg, crystallizing in the undistorted cubic NaTl (B32) type ($a = 7.253$, Å, space group: $Fd3m$), is formed. To our knowledge, this is the first observation of a temperature driven B2/B32 phase transition.

INTRODUCTION

Although all possible compounds between alkali metals and group 13 elements of chemical composition AB (A: alkali metal, B: group 13 element) are not known yet, they have attracted considerable interest as classical examples of »Zintl phases« crystallizing in the »NaTl structure type« (B32), except for LiTl (B2 type, CsCl structure). It was originally proposed by Zintl and Brauer¹ that, in these compounds, an electron transfer from the electropositive alkali metal atoms to the less electropositive atoms of the group 13 elements takes place. As a consequence, the latter act as pseudo group 14 elements in forming a usual sp^3 bonded diamond lattice. This bonding picture, however, has been subject of controversial discussions, in particular among theoreticians (for a summary see Ref. 2). Nevertheless, the concept

TABLE I

Structure types of the known AB compounds
(A: Alkali metal B: group 11, 12, 13 element)

group 11	group 12	group 13
		LiAl, B32 ^{4a}
	LiZn, B32 ¹	LiGa, B32 ^{4a}
	LiCd, B32 ¹	LiIn, B32 ^{4a}
RbAu, B2 ¹²	LiHg, B25	
CsAu, B2 ¹²	α -NaHg, (B2*) ⁹	LiTl, B2 ^{4a}
	β -NaHg, (B32*) ⁺	NaTl
	γ -NaHg, (B32) ⁺	

B2*, B32* distorted B2, B32

⁺ this work

of »Zintl phases«, especially in the extended version of Klemm and Busman,³ turned out to be a very useful tool for a wide range of problems in structural inorganic chemistry (for excellent reviews see Ref. 4).

Replacement of B-atoms by a group 12 element or even by a group 11 element progressively favours the CsCl structure type (B2) over B32 (Table I) due to a complex interplay of different bonding factors. As a consequence, LiZn and LiCd crystallize in the B32 type, whereas LiHg,⁵ CsAu, and RbAu¹² have the B2 structure. Energy differences between B2 and B32 for these compounds are assumed to be small,² thus making predictions nearly impossible. Phase transitions, however, are likely to happen. For group 12 elements, the energetic situation is further complicated by the fact that NaHg, the main subject of this paper, as well as KHg and CsHg are distorted variants of the B2 type, in contrast to LiHg, which shows no distortion.

Whereas KHg⁶ and CsHg^{7,8} correspond to B2 structures with a triclinic distortion characterized by isolated Hg₄ clusters, embedded in a matrix of alkali metal atoms, NaHg crystallizes under normal conditions in an orthorhombically distorted variant of the B2 structure.⁹ The latter is characterized by zig-zag chains of condensed, rectangular Hg₄ clusters isolated from each other by sodium atoms. Idealizing the structure to a certain extent and assuming the Hg-atoms in NaHg (termed α -NaHg in the following text) to form three homonuclear bonds with the neighbouring Hg-atoms, one could call α -NaHg a true Zintl phase in the sense of a formulation Na⁺Hg⁻ (Hg⁻ being a pseudoelement of the main group 13).

Detailed phase analyses and X-ray investigations in the sodium rich part of the system sodium - mercury gave rise to the assumption of an hitherto unknown amalgam near NaHg with the approximate composition Na₇Hg₈.

To our surprise, this assumption turned out to be erroneous and, instead, we found two new high temperature polymorphs of NaHg, one of them a distorted (β -NaHg) and the other an undistorted (γ -NaHg) B32 structure of the classical Zintl type, being however no longer true ZINTL phases with respect to the chemical bonding, because each Hg-atom has now four homonuclear bonds with the neighbouring atoms instead of three as in the low temperature α -phase. To our knowledge, this is the first experimental observation of a temperature driven phase transformation of this type. In this paper, we report the structural and thermodynamical data of the two new NaHg-polymorphs (β/γ) derived by thermal measurements as well as X-ray investigations and discuss their relations to α -NaHg.

EXPERIMENTAL

Gold bronze coloured, air sensitive samples of the composition NaHg with metallic lustre were prepared by a synthetical method starting from the elements and described elsewhere.¹⁰

DSC measurements in the temperature range $293 \text{ K} < T < 500 \text{ K}$ were carried out with a STA/DuPont 900 instrument using sealed aluminium pans with a special inner coating to prevent reaction between the amalgam and aluminium. For X-ray measurements with samples in sealed capillaries, we used a modified high temperature Guinier type camera allowing variable temperatures with a synchronous movement of the X-ray film.¹¹

Table II contains a summary of thermodynamical data for the phase transitions of NaHg. Crystallographic and X-ray data are given in Tables III and IV.

TABLE II

Thermodynamical data for the phase transitions of NaHg with respect to the reduced formula $\text{Na}_{0.5}\text{Hg}_{0.5}$

	α/β	β/γ	γ/melt
$T/^\circ\text{C}$	165(1)	176(1)	215(1)
$\Delta H/\text{kJ mol}^{-1}$	0.16(1)	0.17(1)	5.35(2)
$\Delta S/\text{J mol}^{-1} \text{K}^{-1}$	0.37(1)	0.38(1)	10.96(2)
$v/\text{cm}^3 \text{mol}^{-1}$	30.4(1)/28.3(1)	28.3(1)/28.7(1)	—

* T : transition temperature; ΔH , ΔS : transition enthalpy, transition entropy;
 v : molar volume

** standard deviations of the last digits in the parentheses

RESULTS AND DISCUSSION

When heating a sample of α -NaHg starting from room temperature, one can observe two distinct thermal effects, one at 165 °C and the other at 176 °C, (Figure 1, Table II), indicating two first order transitions below the melting point (215 °C). The transition enthalpies and entropies are comparatively small but in the order of magnitude typical of the polymorphic phase transitions in the solid state. X-ray exposures at a heating rate of 1 K h⁻¹ clearly reflect the reversible phase transitions associated with thermal effects in a significant change of reflection patterns. At 165 °C in a reconstructive transition β -NaHg is formed, which transforms to γ -NaHg at 176 °C in a displacive transition. The powder pattern of β -NaHg can be indexed on the basis of a unit cell, which represents a slight rhombohedral distortion of the cubic cell obtained for γ -NaHg (Tables III and IV).

Due to their first order character, it is not possible to reproduce these phase transitions with single crystal X-ray data; one can, however, show clearly by powder intensity calculations that γ -NaHg has the simple cubic NaTl type structure found frequently for a number of classical Zintl phases, in particular for some related 1:1 compounds (Table I).

TABLE III
Crystallographical data for β - and γ -NaHg

	β -NaHg	γ -NaHg
Space group	$R3m$	$Fd3m$
Z	6	8
Lattice constants/Å		
cubic setting	—	$a = 7.253(4)$
hexagonal setting	$a = 5.071(8)$ $c = 12.668(31)$	$a = 5.129$ $c = 12.563$
rhombohedral setting	$a = 5.138$ $\alpha = 59.130^\circ$	$a = 5.129$ $\alpha = 60^\circ$
Atomic positions	Hg(6c) $z \approx 0.125$ Na(6c) $z \approx 0.375$	Hg(8a) Na(8b)

* Standard deviations of the last digits in the parentheses

TABLE IV

Observed and calculated θ -values (θ_{obs} , θ_{calc}), intensities (I_{obs} , I_{calc}) and Miller Indices (h , k , l) for β -NaHg (upper part) and γ -NaHg (lower part)

θ_{obs}	θ_{calc}	I_{obs}	I_{calc}	h	k	l
β -NaHg						
10.53	10.51	m	350	0	0	3
10.66	10.70	s	1000	1	0	1
17.44	17.45	s	658	1	0	4
17.66	17.69	m	624	1	1	0
20.51	20.55	w	105	0	1	5
20.72	20.75	m	101	1	1	3
			101	1	1	-3
20.89	20.86	w	99	0	2	1
25.31	25.27	vw	130	0	2	4
γ -NaHg						
10.62	10.62	vs	1000	1	1	1
17.51	17.48	s	910	2	2	0
20.62	20.62	m	280	3	1	1
25.15	25.13	w	86	4	0	0
27.56	27.57	w	69	3	3	1
31.31	31.34	w	99	4	2	2
33.49	33.48	vw	23	5	1	1
			8	3	3	3

* $\theta_{\text{max}} = 26^\circ$, Cu $K\alpha_1$, I_{obs} are visually estimated;

** vs = very strong, s = strong, m = medium, w = weak, vw = very weak; I_{calc} are based on the atomic parameters given in Table III, and scaled on a maximum value of 1000

β -NaHg, on the other side, existing only in a small temperature range (Table II) must have a closely related structure distinguished by a slight rhombohedral distortion ($0,87^\circ$) from γ -NaHg. Despite some uncertainty in the precise positional parameters for the Na- and Hg-atoms in β -NaHg, which can be derived from film powder data only, there is no doubt that the mercury atoms in β - and γ -NaHg form a 3-dimensional tetrahedral framework (slightly distorted in β -NaHg) with uniform interatomic distances $d_{\text{Hg-Hg}} = 3.14 \text{ \AA}$ (CN = 4, counting Hg neighbours only; however, the shortest $d_{\text{Na-Hg}} = 3.14 \text{ \AA}$ (4x)). This arrangement is interpenetrated by a corresponding tetrahedral network of sodium atoms with similar interatomic distances $d_{\text{Na-Na}}$ and $d_{\text{Na-Hg}}$. The given distances have to be compared with the corresponding values in α -NaHg ($d_{\text{Hg-Hg}} = 3.05 \text{ \AA}$ (1x), 3.22 \AA (2x), CN = 3, counting Hg neighbours only; however, the shortest $d_{\text{Na-Hg}} = 3.14 \text{ \AA}$).

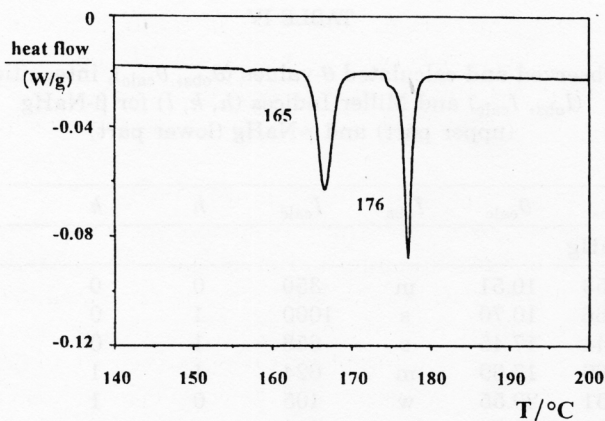


Figure 1. DSC measurement for NaHg in the temperature range $140\text{ }^{\circ}\text{C} < T < 200\text{ }^{\circ}\text{C}$, showing the two endothermic transition peaks at $165\text{ }^{\circ}\text{C}$ and $176\text{ }^{\circ}\text{C}$, heating rate $2\text{ }^{\circ}\text{C min}^{-1}$, sample mass 9.6 mg (due to scaling problems, the strong melting peak at $215\text{ }^{\circ}\text{C}$ is omitted).

It has been shown by extensive theoretical calculations (for a summary see Ref. 2) that the problem of alternative occurrence of the B2 or B32 structure is closely connected to several competing factors. One of them concerns the electrostatic energy term, caused by the above mentioned charge transfer from the alkali metal to group 11, 12, 13 atoms, while another concerns

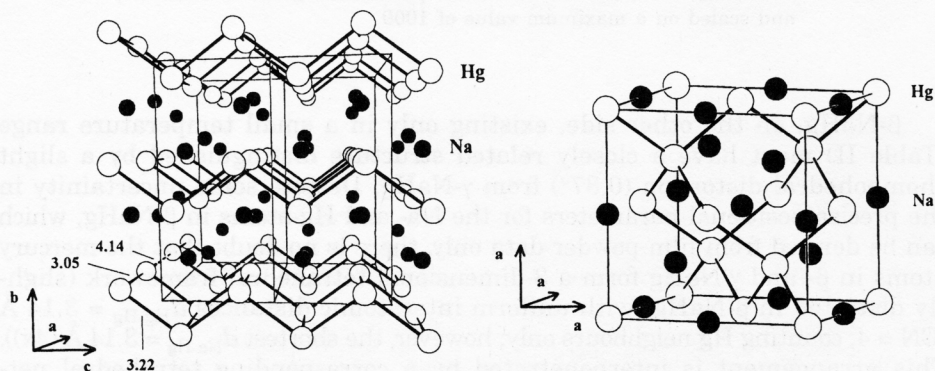


Figure 2. A Comparison of the crystal structures of α -NaHg (left) and γ -NaHg (right), the latter being practically identical to β -NaHg (except for a small rhombohedral distortion).

the covalent bonding forces (sp^3) among the latter. In addition, it was shown that a certain size difference between atoms A and B favours the B32 structure. On the other hand, the increasing size of B is the main reason for the destabilization of B32 so that LiTl¹ crystallizes in B2 and not in B32 as NaTl does.

Although already the molar volume of α -NaHg shows a reduction of $\Delta V = -17\%$, as compared to the sum of the volumes of elements, this value is further reduced to -24% upon formation of the β -phase. The small volume increase for the β/γ -transition (Table II) may be neglected. This finding indicates a more effective packing of the atoms in the high temperature phases (β/γ) than in the low temperature phase (α). It must, however, be stated that the space fillings assuming ideal B2 or B32 structures and Na- and Hg-atoms of equal size should be the same due to the topological equivalence of both structures.²

In general, such a decrease of the molar volume, indicating significant ionic bonding portions, is typical of intermetallic compounds between metals differing markedly in electronegativity. A maximum value of $\Delta V = -39\%$ is reached for CsAu (= Cs⁺Au⁻) when comparing its molar volume with that of the sum of the elements.¹² Indeed, comparable volume effects of approximately 10% in both directions ($-\Delta V$ as well as $+\Delta V$) are found for phase transitions in other sodium amalgams¹³ too. The reasons, however, are different and should be discussed separately in each individual case.

REFERENCES

1. E. Zintl and G. Brauer, *Z. Phys. Chem.* **B20** (1933) 245.
2. N. E. Christensen, *Phys. Rev.* **B32** (1985) 207.
3. W. Klemm and E. Busmann, *Z. Anorg. Allg. Chem.* **319** (1963) 207.
4. a) H. Schäfer, B. Eisenmann, and W. Müller, *Angew. Chem.* **85** (1973) 742;
b) H. Schäfer and B. Eisenmann, *Rev. Inorg. Chem.* **3** (1981) 29; c) R. Nesper, *Progr. Sol. State Chem.* **20** (1990) 1.
5. E. Zintl and G. Brauer, *Z. Phys. Chem.* **B20** (1933) 254.
6. N. C. Baenziger and W. J. Nielsen, *Acta Cryst.* **7** (1954) 277.
7. H. J. Deiseroth and A. Strunck, *Angew. Chem.* **99** (1987) 701.
8. H. J. Deiseroth, A. Strunck, and W. Bauhofer, *Z. Anorg. Allg. Chem.* **575** (1989) 31.
9. H. J. Deiseroth, A. Stupperich, R. Pankaluoto, and N. E. Christensen, *Z. Anorg. Allg. Chem.* **597** (1991) 41.
10. H. J. Deiseroth, A. Strunck, and W. Bauhofer, *Z. Anorg. Allg. Chem.* **558** (1988) 128.
11. A. Simon, *J. Appl. Cryst.* **3** (1970) 11; *J. Appl. Cryst.* **4** (1971) 138.
12. U. Zachwieja, *Z. Anorg. Allg. Chem.* **619** (1993) 1095.
13. M. Rochnia, Dissertation, Universität-GH Siegen, 1994.

SAŽETAK

Polimorfija NaHg: Prvo eksperimentalno opažanje reverzibilnog prijelaza B2 (CsCl) - B32 (NaTl) izazvanoga promjenom temperature*Matthias Rochnia i Hans-Jörg Deiseroth*

Na temelju rentgenske difrakcije i termičkih istraživanja nađeno je da se intermetalni spoj NaHg javlja u tri različite modifikacije (α -, β - i γ -NaHg). Ranije poznata niskotemperaturna modifikacija α -NaHg kristalizira u deformiranoj rombskoj strukturi tipa CsCl (B2). Prijelazom prvog reda pri 165 °C, α -NaHg se transformira u β -NaHg, blago deformiranu rombsku strukturu tipa NaTl (B32) ($a = 5.071(8)$, $c = 12.668(31)$ Å, prostorna grupa $R3m$). Postupnim prijelazom prvoga reda pri 176 °C nastaje γ -NaHg koji kristalizira u kubičnoj strukturi tipa NaTl (B2) ($a = 7.253$ Å, prostorna grupa: $Fd3m$). Prema našem znanju to je prvi opaženi prijelaz faze B2 u fazu B32 izazvan promjenom temperature.