Journal of Solid State Chemistry **147**, 177–184 (1999)
Article ID jssc.1999.8209, available online at http://www.idealibrary.com on IDEAL®

$NaK_{29}Hg_{48}$: A Contradiction to or an Extension of Theoretical Concepts to Rationalize the Structures of Complex Intermetallics?

Hans-Jörg Deiseroth and Erik Biehl

Anorganische Chemie, Universität-GH Siegen, Siegen, Germany
E-mail: deiseroth@chemie.uni-siegen.de

Received November 4, 1998; in revised form February 2, 1999; accepted February 3, 1999

IN MEMORIAM OF PROF. DR. JEAN ROUXEL

$NaK_{29}Hg_{48}$ is a new silver metallic, air-sensitive ternary alkali metal amalgam with metallic properties. It crystallizes in space group *Pm*$\bar{3}$*n* (No. 223, $Z = 2$, $a = 1685.3(2)$ pm) and shows a superconducting phase transition at 2.5 K. Its crystal structure is characterized by novel icosahedral Hg_{12} clusters centered by Na atoms and hexagonal antiprismatic Hg_{12} clusters ("drums") centered by K atoms. Both cluster types are embedded in a matrix of K atoms. With respect to the topology of the cluster centers the three-dimensional arrangement corresponds to the A15 structure type (Nb_3Sn). The crystal structure of $NaK_{29}Hg_{48}$ is closely related to that of the complex intermetallic phases $A_3Na_{29}In_{48}$ (A = K, Rb, Cs) and others. It is an unexpected electron deficient borderline case with respect to electron counting rules (Wade's rules and Zintl–Klemm concept), which were successfully applied to explain the occurence of icosahedral and hexagonal antiprismatic In_{12}/Tl_{12} clusters in the latter two compounds. © 1999 Academic Press

Key Words: **amalgam; alloy; crystal structure; mercury clusters.**

INTRODUCTION

The complex and puzzling cluster chemistry of intermetallic compounds formed by alkali metals, group 13 elements (Ga, In, Tl) like $K_3Na_{26}In_{48}$, $K_{49}Tl_{108}$ (1–3), and others like $Na_{23}K_9Tl_{13.5}$, $A_{15}Tl_{27}$ (A = Rb, Cs), NaK_9Tl_{13}, CsTl, and $Na_7In_{11.8}$ (4–14, 29) synthesized in recent years could be rationalized elegantly by presuming an electron transfer from the alkali metals to the group 13 element atoms and applying two successful classical concepts: (1) the Zintl–Klemm concept (15–17, 29) and (2) Wade's rules (18–20). Both concepts are based on specific valence electron counting using mainly *p*- and/or *d*-electrons and either "pseudo-elements" (Zintl–Klemm) or suitable molecular orbitals (Wade's rules) as helpful arguments for rationalizing the variety of cluster geometries formed by the group 13 elements in those solids

With $NaK_{29}Hg_{48}$ we present a new compound, in which the group 13 metal (In) of $K_3Na_{26}In_{48}$ is completely replaced by a group 12 metal (Hg). As a consequence of this replacement one should expect structural differences due to the fact that the number of available valence electrons is drastically reduced (In, *three*; Hg, *two* valence electrons). Surprisingly, however, the two solids are *isostructural* (except an additional centering of one of the polyhedra) and differ only slightly in their structural characteristics (lattice constants, interatomic distances, etc.).

This unexpected contradiction serves as a main background in this paper for discussions based on comparisons between $NaK_{29}Hg_{48}$ and the above mentioned $A_3Na_{29}Hg_{48}$. It can be taken as an occasion to reexamine or modify the above mentioned rules with respect to those intermetallics containing Ga, In, or Tl, which seemed to be good candidates for a successful application. It might be that other important arguments have been missed.

EXPERIMENTAL

Preparation

A few crystals of $NaK_{29}Hg_{48}$ were first obtained in the course of systematic studies on potassium amalgams by erroneously assuming the chemical composition to be $K_{29}Hg_{48}$. Intensive efforts, however, to synthesize greater quantities of "$K_{29}Hg_{48}$" showed peculiarly low yields. Subsequent careful analyses (21) based on different methods soon showed that the starting potassium sample was slightly contaminated with sodium. Further experiments now adding stoichiometric quantities of Na (see below) yielded $NaK_{29}Hg_{48}$ free of impurities, which can be shown clearly by high-resolution X-ray diffraction (Fig. 1).

$NaK_{29}Hg_{48}$ can be obtained using a special experimental glass setup described elsewhere (22) by mixing stoichiometric quantities of Na (Merck $> 99\%$), K (Fluka $> 99\%$, purified by segregation), and Hg (Degussa, 99,999%) and

0022-4596/99 $30.00

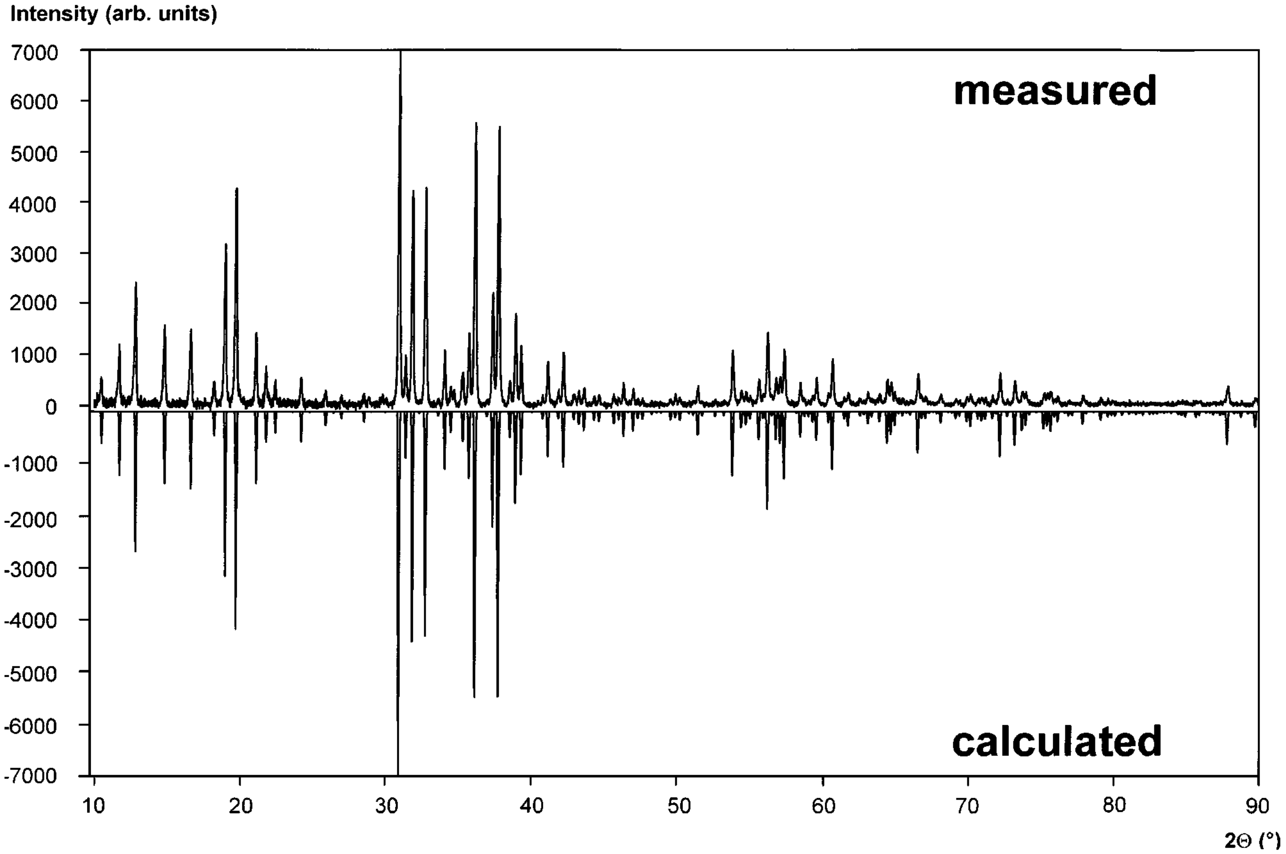


FIG. 1. X-ray powder diagram of $NaK_{29}Hg_{48}$ (Cu$K\alpha_1$, STOE StadiP, 0.02°/step).

heating the mixture up to 520 K to ensure the formation of a homogeneous melt. The sample is subsequently cooled down to 450 K and kept at this temperature for 4 weeks. The product that appears is silver metallic, is highly air sensitive, and contains regularly shaped crystals (Fig. 2) suitable for single-crystal investigations. Crystals were selected under inert gas by using an optical microscope and were mechanically fixed in X-ray glass capillaries. Diffraction data for single crystals of $NaK_{29}Hg_{48}$ were collected on a CAD4 diffractometer at 290 K with monochromatized Mo$K\alpha$ radiation ($2\theta_{max} = 50°$). Relevant X-ray data and positional and isotropic displacement parameters are summarized in Tables 1 and 2. A selection of interatomic distances is given in Table 3. Magnetic measurements were carried out in a SQUID magnetometer (MPMS-7, Quantum Design, San Diego, CA) by filling the microcrystalline $NaK_{29}Hg_{48}$ samples in gelatin containers under He gas. Figure 3 shows the results of magnetic measurements for two different temperature ranges.

RESULTS AND DISCUSSON

In $NaK_{29}Hg_{48}$ as well as $A_3Na_{26}In_{48}$ (1,2) icosahedral *closo*-clusters (two per unit cell) and hexagonal antiprismatic *arachno*-clusters ("drums," six per unit cell) are regarded as main building units (Fig. 4). They are embedded in a matrix of alkali metal atoms.

In contrast to the icosahedral *closo*-In_{12} in $A_3Na_{26}In_{48}$ the corresponding icosahedral *closo*-Hg_{12} in $NaK_{29}Hg_{48}$ are centered by Na atoms thus forming $NaHg_{12}$ units.The hexagonal antiprismatic *arachno*-In_{12} clusters, which are centered by Na atoms in the case of $A_3Na_{26}In_{48}$ ($NaIn_{12}$) and by K atoms in the case of $NaK_{29}Hg_{48}$ (KHg_{12}), can be derived from a hypothetical (centered) *closo*-icosatetrahedron KHg_{14} ($NaIn_{14}$) by removing two apical Hg (In) atoms.

All 12 vertices of both Hg_{12} cluster types are bonded via short intercluster bonds, Hg–Hg, to neighboring clusters (Figs. 4 and 5) thus forming a complete three-dimensional network of Hg–Hg contacts. The lengths of these contacts correspond roughly to the avarage $d_{Hg\text{–}Hg}$ in elemental α-Hg (23) and to typical $d_{Hg\text{–}Hg}$ in other alkali metal amalgams (24). The arrangement of clusters corresponds to the $A15$ structure (Nb_3Sn) with Nb/Sn replaced by the hexagonal antiprisms/icosahedra. Corresponding statements are valid for the $A_3Na_{29}In_{48}$ compounds.

$NaK_{29}Hg_{48}$ appears metallic and is diamagnetic with a slight temperature dependence. It shows a steep decrease

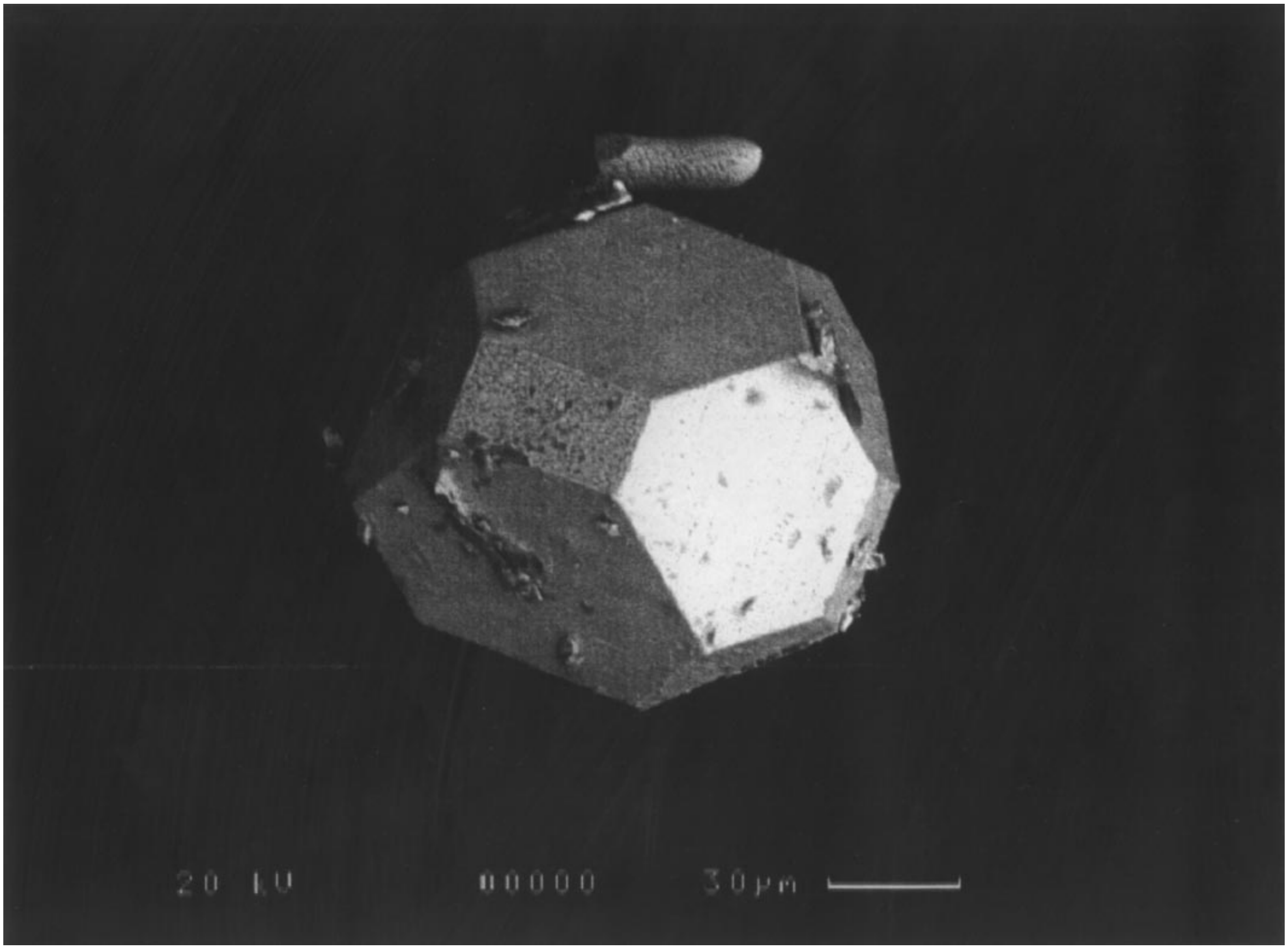


FIG. 2. A selected single crystal of $NaK_{29}Hg_{48}$ with the shape of a truncated octahedron viewed in the scanning electron microscope.

of the diamagnetic susceptibilty below 2.9 K (Fig. 3) indicating superconductivity ("Meissner effect").

As mentioned above, $NaK_{29}Hg_{48}$ differs from $A_3Na_{26}In_{48}$ only in so far as the *closo*-Hg_{12} icosahedra are *centered* by Na atoms whereas the *closo* In_{12} icosahedra are not. In all further topological aspects the structures of $NaK_{29}Hg_{48}$ and $A_3Na_{26}In_{48}$ are identical.

In particular we find the *intracluster* distances $d_{Hg\text{–}Hg}$ to be *longer* than the *intercluster* ones (exo-bonds) in complete accordance with the corresponding situation in $A_3Na_{26}In_{48}$.

Each icosahedron $NaHg_{12}$ is connected to *twelve* neighbored hexagonal antiprisms KHg_{12} by 12 contacts $d_{Hg\text{–}Hg} = 291.7$ pm ($d_{In\text{–}In} = 291.2$ pm). These are the shortest $d_{Hg\text{–}Hg}$ in the structure but are, however, still significantly longer than typical covalent single bonds Hg–Hg in, e.g., Hg(I) halides (255 ± 10 pm (25)). Each hexagonal antiprism KHg_{12} is connected to *four* icosahedra with $d_{Hg\text{–}Hg} = 291.7$ pm ($d_{In\text{–}In} = 291.2$ pm) and to *eight* antiprisms with $d_{Hg\text{–}Hg} = 318.1$ pm ($d_{In\text{–}In} = 305.3$ pm).

Intracluster distances $d_{Hg\text{–}Hg}$ for the icosahedra (Hg1 only, Fig 4) are 307.1 pm (292.7, $1\times$) and 326.3 pm (300 pm, $4\times$) per Hg1 atom (corresponding values $d_{In\text{–}In}$ for $K_3Na_{26}In_{48}$ and multiplicity in parentheses). In addition one intercluster bond of 291.7 pm (291.2) extends from every Hg1 to a neighbored icosahedron as already mentioned above.

The distances $d_{Na\text{–}Hg1} = 306.5$ pm between the center Na and surface Hg atoms (Hg1) in the $NaHg_{12}$ icosahedra are relatively short in comparison to $d_{Na\text{–}Hg}$ in other sodium amalgams ((24), Na_8Hg_3, $d_{Na\text{–}Hg} > 314.6$ pm; NaHg, $d_{Na\text{–}Hg} > 314.8$ pm; $NaHg_2$, $d_{Na\text{–}Hg} > 316$ pm), which, however, never contain this unique cluster. In summary one can state that there is a tendency for the *intracluster bonds* $d_{Hg\text{–}Hg}$ of the icosahedra to be slightly longer than $d_{In\text{–}In}$ although indium atoms are *larger* than mercury atoms (metallic radii are 167 pm for In and 155 pm for Hg (30)).

TABLE 1
Summary of Relevant X-Ray Data for $NaK_{29}Hg_{48}$[a]

Formula/Pearson code	$NaK_{29}Hg_{48}$ [$cP156$]
Space group	$Pm\bar{3}n$, No. 223
Lattice constant (pm)	$a = 1685.3(2)$
Volume (pm^3)	4787.25×10^6
Formula units	2
Crystal size (mm^3)	$0.1 \times 0.1 \times 0.2$
Density (g/cm^3)	7.748
Linear absorption coefficient $\mu_{MoK\alpha}$ (mm^{-1})	778.94
Temperature (K)	298
Diffractometer	Enraf-Nonius CAD4 Mo$K\alpha$ ($\lambda = 0.71073$ Å), graphite monochromator, scintillation counter
Data range	$-20 < h < 20$, $-20 < k < 20$, $0 < l < 20$
$2\theta_{max}$ (°)	50
Scan type	ω-scan
Absorption correction	Ψ scans
Refinement	NRCVAX (28)
Number of reflections	12,880
Number of reflections used	789
Number of reflection with $I_0 > 2\sigma(I_0)$	440
R_F ($I_0 > 2\sigma(I_0)$)/R_F (all reflections)	0.0618/0.0618
R_W ($I_0 > 2\sigma(I_0)$)/R_W (all reflections)	0.0791/0.0791
Extinction coefficient	0.00772
Residual electron density $\Delta\rho_{max}/\Delta\rho_{min}$ (e/Å^3)	4.49/−3.81

[a] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe (D-76344 Eggenstein-Leopoldshafen, Germany), on quoting the depository numbers CSD-410570 ($NaK_{29}Hg_{48}$).

This may be taken as an indication for the significantly lower number of valence (bonding) electrons available in $NaK_{29}Hg_{48}$ in comparison to $K_3Na_{26}In_{48}$ (see "Electron Counting and Critical Discussion of Interatomic Distances" below). It is, however, difficult to separate this effect from the distance expansion triggered by the Na atoms centering the Hg_{12} icosahedra but *not* the In_{12} icosahedra.

Intracluster distances $d_{Hg\text{–}Hg}$ (Hg2 and Hg3) for Hg2 in the hexagonal antiprisms (Fig. 4) are $d_{Hg2\text{–}Hg3} = 318.6$ pm (304.7, 2×) and 328.2 pm (314.8, 2×). In addition one intercluster bond $d_{Hg2\text{–}Hg1} = 291.7$ pm (291.2) to a neighboring icosahedron exists. The corresponding distances for Hg3

TABLE 2a
Atomic Coordinates and Displacement Parameters for $NaK_{29}Hg_{48}$ (10^4 pm^2)

Atom	Site	Site symmetry	x	y	z	U_{eq}
Hg1	24k	$m..$	0.1575(1)	0.0911(1)	0	0.039(1)
Hg2	24k	$m..$	0.3140(1)	0.1652(1)	0	0.046(1)
Hg3	48l	l	0.3274(1)	0.3273(1)	0.0961(1)	0.036(1)
Na	2a	$m\bar{3}.$	0	0	0	0.069(4)
K1	6b	$mmm..$	0	$\frac{1}{2}$	$\frac{1}{2}$	0.054(5)
K2	24k	$m..$	0.3671(2)	$\frac{1}{2}$	0.2048(2)	0.046(5)
K3	16i	$.3.$	0.3119(3)	x	x	0.062(1)
K4	6d	$\bar{4}m.2$	1/2	0	$\frac{1}{4}$	0.046(4)
K5	6c	$\bar{4}m.2$	0	$\frac{1}{2}$	$\frac{1}{4}$	0.069(4)

TABLE 2b
Displacement Parameters U_{ij}[a] for $NaK_{29}Hg_{48}$ (10^4 pm^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg1	0.0335(5)	0.0378(4)	0.0447(5)	−0.0045(4)	0	0
Hg2	0.0443(4)	0.0441(6)	0.0511(5)	0.0106(3)	0	0
Hg3	0.0526(4)	0.0452(3)	0.0428(4)	0.0036(2)	−0.0015(3)	−0.0023(3)
Na	0.069(8)	U_{11}	U_{11}	0	0	0
K1	0.048(5)	0.056(7)	0.059(7)	0	0	0
K2	0.046(2)	0.066(3)	0.026(2)	0	0.011(1)	0
K3	0.063(1)	U_{11}	U^{11}	0.019(1)	U_{12}	U_{12}
K4	0.058(4)	U^{11}	0.029(5)	0	0	0
K5	0.026(3)	U^{11}	0.087(8)	0	0	0

[a] U_{ij} is defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2hka^*b^*U_{12} + \cdots)$.

TABLE 3
Main Interatomic Distances (pm) in $NaK_{29}Hg_{48}$

Hg1–Hg2[a]	291.7(1)	1×	K1–K2	411.4(2)	4×
Hg1–Hg1	307.1(1)	1×	K1–Hg2	419.2(1)	4×
Hg1–Hg1	326.3(1)	4×	K1–Hg3	421.2(1)	8×
Hg1–Na	306.5(1)	1×	K1–K4	421.3(1)	4×
Hg1–K2	346.4(4)	1×			
Hg1–K2	357.2(2)	2×	K2–Hg1	346.4(3)	1×
Hg1–K3	360.4(7)	2×	K2–Hg3	350.3(3)	2×
			K2–Hg1	357.2(4)	2×
Hg2–Hg1[a]	291.7(1)	1×	K2–Hg2	358.6(3)	2×
Hg2–Hg3	318.6(1)	2×	K2–Hg3	369.7(4)	2×
Hg2–Hg3	328.2(1)	2×	K2–K3	376.4(7)	2×
Hg2–K5	344.6(1)	2×	K2–K4	397.7(4)	1×
Hg2–K2	358.6(3)	1×	K2–K1	411.4(3)	1×
Hg2–K2	375.7(4)	2×	K2–K2	447.8(9)	1×
Hg2–K3	383.3(1)	1×			
Hg2–K5	419.2(1)	1×	K3–Hg1	360.3(7)	3×
			K3–K3	361(1)	1×
Hg3–Hg3[a]	318.1(2)	1×	K3–Hg3	365.6(4)	3×
Hg3–Hg3	318.5(1)	1×	K3–Hg3	366.4(4)	3×
Hg3–Hg2	318.6(1)	1×	K3–K2	376.4(3)	3×
Hg3–Hg3	323.9(1)	1×	K3–Hg2	383.4(1)	3×
Hg3–Hg2	328.2(1)	1×			
Hg3–K2	350.3(2)	1×	K4–Hg3	357.7(1)	8×
Hg3–K4	357.5(1)	1×	K4–K2	397.7(4)	4×
Hg3–K5	357.7(1)	1×	K4–K2	421.3(1)	2×
Hg3–K3	365.6(4)	1×			
Hg3–K3	366.5(4)	1×	K5–Hg2	344.6(6)	4×
Hg3–K2	369.7(4)	1×	K5–Hg3	357.5(1)	8×
			K5–K1	421.3(1)	2×
Na–Hg1	306.5(1)	12×			

[a] Intercluster exo-bonds.

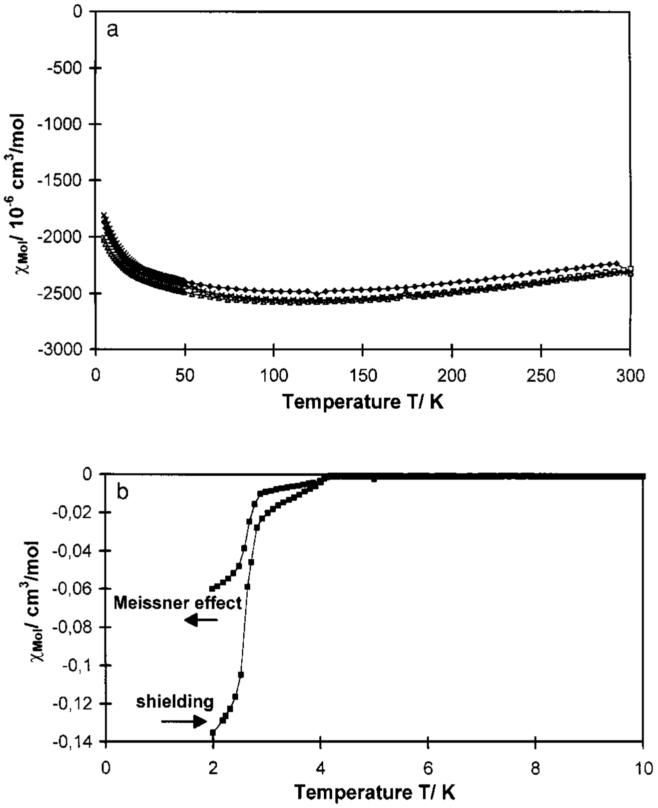


FIG. 3. The magnetic susceptibilty of $NaK_{29}Hg_{48}$ in two different temperature ranges. (a) magnetic field (**H**): $1\ T < \mathbf{H} < 7\ T$; (b) 0.001 T, cooling in field (Meissner effect), cooling without field (shielding).

are $d_{Hg3\text{-}Hg3} = 323.9/318.5$ pm (314.8/304.7, 1 × each) and $d_{Hg3\text{-}Hg2} = 328.2/318.1$ pm (312.1/306.2, 1 × each). Again an additional intercluster bond $d_{Hg3\text{-}Hg3}$ to a neighbored hexagonal antiprism exists.

The distances between K5 in the center of the hexagonal antiprism and the peripheral Hg atoms are $d_{K5\text{-}Hg2} = 344.6$ pm (323.3, 6 ×) and $d_{K5\text{-}Hg3} = 357.5$ pm (339.2, 6 ×). They are in accordance with typical distances $d_{K\text{-}Hg}$ (24) in KHg ($d_{K\text{-}Hg} > 356$ pm), KHg_2 ($d_{K\text{-}Hg} > 352$ pm), K_5Hg_7 ($d_{K\text{-}Hg} > 352$ pm), K_7Hg_{31} ($d_{K\text{-}Hg} > 345$ pm), K_2Hg_7 ($d_{K\text{-}Hg} > 355$ pm), KHg_{11} ($d_{K\text{-}Hg} > 364$ pm), although none of these solids contains such unusual clusters.

Further structural discussions including the K atoms (K1 to K4) and analyzing various topological aspects of the highly complex and fascinating structure as, e.g., the relationship to the clathrate-I type and to the Samson polyhedra in $Li_{13}Cu_6Ga_{21}$ are given elsewhere (1, 2) for $K_3Na_{26}In_{48}$ and can be fully transferred to $NaK_{29}Hg_{48}$ by replacing In with Hg and taking into account that the Hg_{12} icosahedra are centered by Na atoms whereas the In_{12} icosahedra are not. The same holds for the individual coordination polyhedra of the K and Hg atoms.

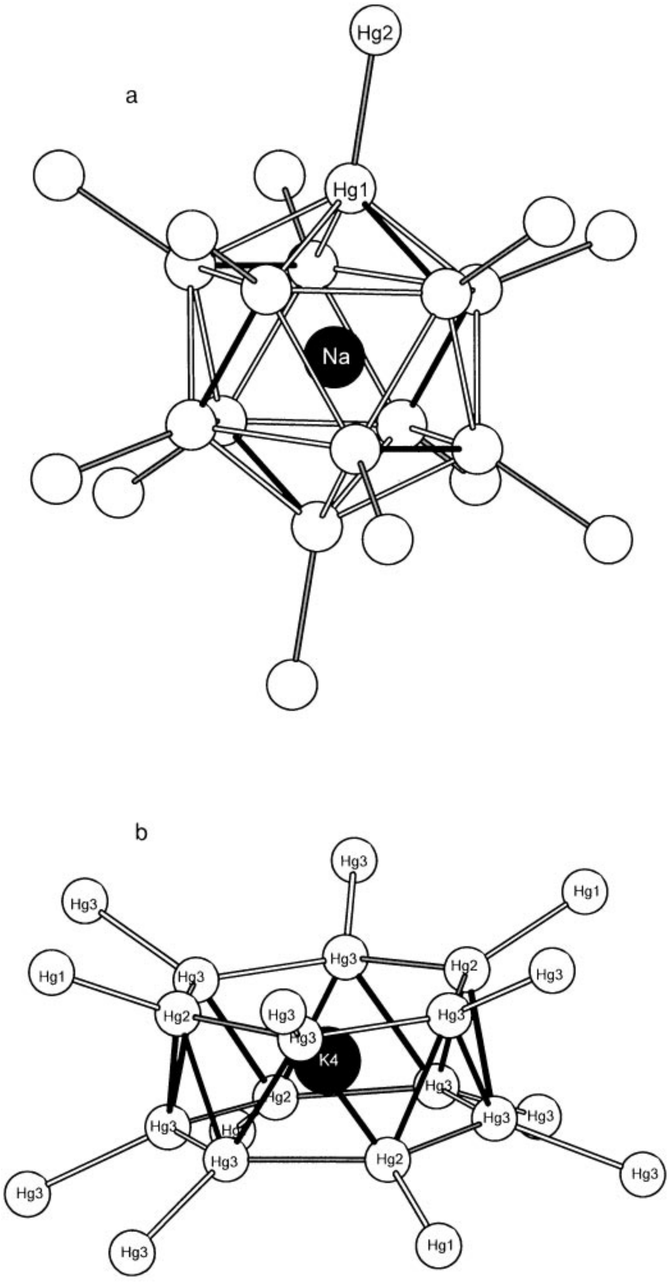
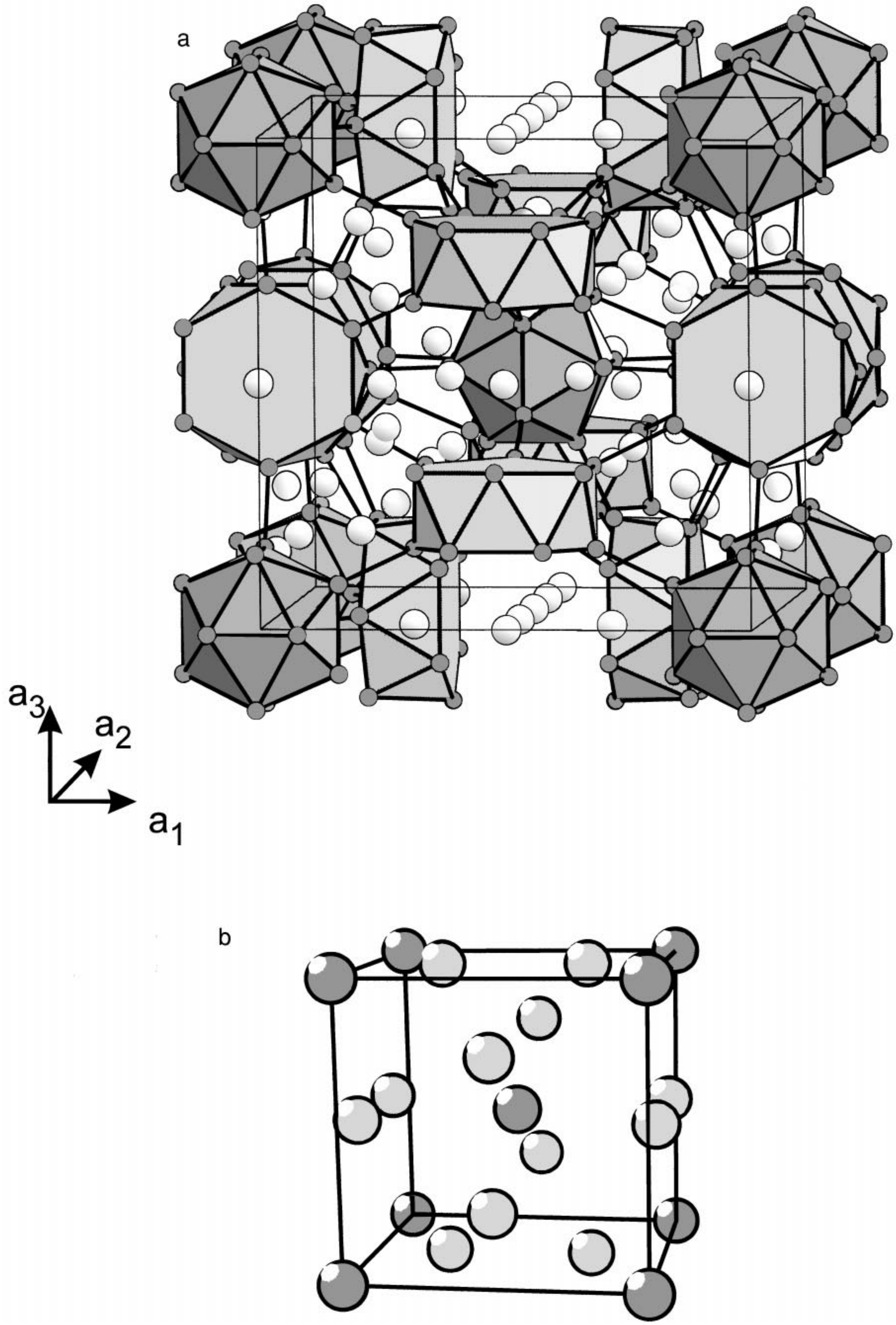


FIG. 4. *Closo*-$NaHg_{12}$ icosahedra (a) and *arachno*-KHg_{12} hexagonal antiprisms (b) in $NaK_{29}Hg_{48}$ (solid and empty atom connection lines indicate different bond lengths).

Electron Counting and Critical Discussion of Interatomic Distances

On the basis of the assumption of a significant electron transfer from Na/K to In in the sense of the Zintl–Klemm concept and according to the application of Wade's rules as discussed in (1) and (2) each of the two *closo*-Hg_{12} per unit cell in $NaK_{29}Hg_{48}$ requires 26 skeletal and 12 exo-bond


a
a_3
a_2
a_1
b

electrons. On the other hand, each of the six *arachno*-Hg_{12} requires 30 skeletal and 12 exo-bond electrons. In this picture all exo-bonds are assumed to be classical 2-electron–2-center bonds. The total number of necessary valence electrons to fill all cluster orbitals and 2-electron–2-center exo-bonds thus becomes 328 (232 e^- for 116 skeletal and 96 e^- for the 48 intercluster bonds) which has to be compared with 252 valence electrons provided by the sum of all alkali metal and mercury atoms (*one* per alkali metal atom, *two* per mercury atom). The complementary calculation for $A_3Na_{26}In_{48}$ (counting *three* valence electrons per indium atom) results in 346 available valence electrons. This number is more than sufficient to fill all inter- and intracluster bonds. The 18 *excess* electrons can be regarded as delocalized in a conduction band consistent with the observed metallic properties of $A_3Na_{26}In_{48}$. But how to treat the *deficiency* of 76 valence electrons in $NaK_{29}Hg_{48}$?

Indeed from the above discussion of interatomic distances small but significant differences between the two compounds become obvious. Although the atomic radius of Hg is slightly smaller than that of In (Hg, 150.3 pm; In, 162.6 pm) the distances Hg-Hg in $NaK_{29}Hg_{48}$ tend, with one exception, to be *greater* than In–In in $A_3Na_{26}In_{48}$. The exception concerns the intercluster distances between icosahedra and hexagonal antiprisms, which are nearly equal for In–In and Hg-Hg. All other comparable distances $d_{\text{Hg-Hg}}$ are significantly *greater* than $d_{\text{In-In}}$. The situation is particularly puzzling for the $NaHg_{12}$ and In_{12} icosahedra, respectively. One has to wonder whether the inter cluster distances $d_{\text{Hg-Hg}}$ are greater than $d_{\text{In-In}}$ *due* to the central Na or whether the electron deficiency *weakens* the Hg–Hg cluster bonds to an extend, that a central Na atom now fits into the enlarged Hg_{12} clusters! Similarly puzzling is the comparison of interatomic distances for the hexagonal antiprisms Hg_{12} and In_{12}. Again one could argue that the Hg–Hg cluster bonds are so weak that large K atoms fit into the enlarged Hg_{12} clusters in contrast to the In_{12} clusters where only small Na atoms fit.

Moreover, it is difficult to estimate the effect of the matrix of K atoms in $NaK_{29}Hg_{48}$ embedding the clusters in comparison to the matrix of Na atoms in $A_3Na_{26}In_{48}$. Generally one would expect a stabilizing effect for both types of highly electron deficient Hg_{12} clusters due to the greater tendency to transfer electrons from K to Hg than from Na to In. Due to earlier studies of the system Na– K (26) and our present knowledge of the system K–Hg the existence of binary $Na_{30}Hg_{48}$ or $K_{30}Hg_{48}$ (M_5Hg_6) is most unlikely.

One objection against the simple model for chemical bonding in $A_3Na_{26}In_{48}$ and $NaK_{29}Hg_{48}$ based on the electron counting rules discussed above comes from preliminary theoretical calculations of the electronic structure (27) for the latter compound. These calculations give significant evidence for the *s*-valence states of K as well as the *p*-valence states of Hg to be partly populated by electrons. Thus the assumption of a complete electron transfer from K to Hg cannot be valid.

CONCLUSIONS

$NaK_{29}Hg_{48}$ is a unique ternary amalgam that consists of centered $NaHg_{12}$ icosahedra and centered KHg_{12} hexagonal antiprisms ("Wade clusters") embedded in a matrix of K atoms. In contrast to a series of indium compounds ($A_3Na_{26}In_{48}$: $A = K$, Rb, Cs), which are structurally very similar, the application of Wade's rules to $NaK_{29}Hg_{48}$ is questionable and predicts a significant deficiency of valence electrons. The deficiency is reflected in geometrical details of the atomic arrangement in particular with respect to selected interatomic distances.

ACKNOWLEDGMENTS

The support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. The authors thank Dr. R. Kremer (Max Planck Institut für Festkörperforschung, Stuttgart) for measurements of the magnetic susceptibilities.

REFERENCES

1. W. Carrillo-Carera, N. Caroca-Canales, K. Peter, and H. G. v. Schnering *Z. Anorg. Allg. Chem.* **619,** 1556 (1993).
2. S. C. Sevov and J. D. Corbett, *Inorg. Chem.* **32,** 1612 (1993).
3. G. Cordier and V. Müller, *Z. Naturforsch. B* **48,** 1035 (1993).
4. Z.-C. Dong and J. D. Corbett, *Inorg. Chem.* **35,** 3107 (1996).
5. Z.-C. Dong and J. D. Corbett, *Inorg. Chem.* **35,** 1444 (1996).
6. Z.-C. Dong and J .D. Corbett, *Inorg. Chem.* **35,** 2301 (1996).
7. G. Cordier and V. Müller, *Z. Naturforsch. B* **50,** 23 (1995).
8. G. Cordier and V. Müller, *Z. Naturforsch. B* **49,** 935 (1994).
9. S. C. Sevov and J. D. Corbett, *Science* **262,** 880 (1993).
10. W. Blase, G. Cordier, V. Müller, U. Häußermann, R. Nesper, and M. Somer *Z. Naturforsch. B* **48,** 754 (1993).
11. S. C. Sevov and J. D. Corbett, *J. Sol. State Chem.* **103,** 114 (1993).
12. G. Cordier and V. Müller, *Z. Kristallog.* **205,** 306 (1993).
13. S. C. Sevov and J. D. Corbett, *Inorg. Chem.* **31,** 1895 (1992).
14. W. Blase and G. Cordier, *Z. Naturforsch. B* **44,** 1479 (1989).
15. H. Schäfer and B. Eisenmann, W. Müller, *Angew. Chem.* **85,** 742 (1973).
16. W. Klemm and E. Busmann, *Z. Anorg. Allg. Chem.* **319,** 297 (1963).
17. H. Schäfer, *Annu. Rev. Mater. Sci.* **15,** 1 (1985).
18. K. Wade, *Adv. Inorg. Chem. Radiochem.* **18,** 1 (1976).
19. C. Belin and R. Ling, *J. Solid State Chem.* **48,** 40 (1983).

FIG. 5. The crystal structure of $NaK_{29}Hg_{48}$ (a) in comparison with the arrangement of atoms in the A15 (Nb_3Sn) type structure (b) (*closo*-$NaHg_{12}$, dark gray polyhedra; arachno-KHg_{12}, light gray polyhedra; K, light gray balls).

20. C. Belin and M. Tillard-Charbonnel, *Progr. Sol. State Chem.* **22,** 59 (1993).
21. E. Biehl, Ph.D. thesis, University of Siegen, Germany, 1998.
22. H. J. Deiseroth, A. Strunck, and W. Bauhofer, *Z. Anorg. Allg. Chem.* **558,** 128 (1988).
23. J. Donohue, "The structures of the elements," p. 231. J. Wiley & Sons, New York, 1974.
24. H. J. Deiseroth, *Progr. Solid State Chem.* **25,** 73 (1997).
25. N. J. Calos, C. H. L. Kennard, and R. L. Davis, *Z. Kristallogr.* **187,** 305 (1989).
26. H. J. Deiseroth, E. Biehl, and M. Rochnia, *J. Alloys Compds* **246,** 80 (1997).
27. E. Biehl and H. J. Deiseroth, to be published.
28. E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee, and P. S. White, *J. Appl. Crystallogr.* **22**, 384 (1989).
29. S. M. Kauzlarich (Ed.), "Chemistry Structure and Bonding of Zintl Phases and Ions," p. 139. VCH Publishers, New York, 1996.
30. A. F. Wells, "Structural Inorganic Chemistry," 5th ed., p. 1288. Clarendon Press, Oxford, 1984.