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Participation of Sodium in the Bonding of Anionic Networks: Synthesis, Structure, and Bonding of Na_3MIn_2 (M = Au, Ag)

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Two isostructural compounds Na_3MIn_2 (M = Au, Ag) with a $NiTi_2$-type structure (*Fd*-3*m*) were synthesized via typical high-temperature reactions. The anionic M–In structure consists of tetrahedral star building units $[In_4M_{4/2}]$ (TS) that are connected into a three-dimensional framework via shared TS vertexes, with the Na atoms filling the cages. On the basis of TB-LMTO-ASA calculations, the electronic structures of both compounds show substantial participation of sodium in the overall bonding of the structure. Compared with the Ag compound, relativistic effects in the Au phase appear to be significant, as shown in the M–M and M–Na bond length decreases of 0.03–0.04 Å.

Alkali or alkaline-earth metals react with many post-transition elements to form a large number of phases with highly diverse structural chemistries.[2] The structures of many of these compounds are rationalized by the Zintl−Klemm concepts by assuming the more-electropositive components, hence the alkali, alkaline-earth, etc. metals, lose their valence electrons to the post-transition elements.[3] Therefore, the bonding situation in these phases is often simply characterized in terms of covalent interactions within the anionic (post-transition element) part of the structures, whereas ionic bonding supposedly governs the cation−anion interactions.

However, recent studies have revealed that the anionic substructures in some compounds are far more diverse and beyond the grasp of the original Zintl−Klemm concepts. The interactions between the anionic and the cationic parts of the structures may play an important role in the stabilities of these phases, and the assumed electron transfer is far overstated and mixing is ignored. For example, appreciable d-orbital mixing from alkaline-earth or rare-earth metal cations with anion states determine decisively the properties of the supposed Zintl phases Ca_5Ge_3 and La_3In_5, making them metallic.[4] In K_3Bi_2 and K_5Bi_4, the alkali-metal and bismuth orbitals mix considerably, providing for a large covalent bonding contribution to the stability of the compounds.[5] Strongly bonding Na−Sb interactions in the metallic Na_6TlSb_4 clearly are manifest in generating an additional band for the extra pair of electrons.[6] We report here the syntheses, structures, and electronic structures of two novel compounds, Na_3AuIn_2 and Na_3AgIn_2, in which substantial participation of sodium in the overall bonding of the structure can be demonstrated. To our knowledge, Na_3AgIn_2 is the first compound in the Na−Ag−In system, and Na_3AuIn_2 is the fourth compound in the Na−Au−In system following $NaAuIn_2$, $Na_2Au_6In_5$, and $Na_8Au_{11}In_6$.[7] Both compounds exhibit a unique framework.

The title compounds were synthesized via typical high-temperature reactions.[8] A quenching of the melts from high temperature is necessary to get pure phases of both compounds, whereas a slow cooling process gives mainly the Bergman-type phase,[9] $Na_{13}(MIn)_{27}$.[10] The structures of Na_3AuIn_2 and Na_3AgIn_2 were determined by single-crystal[11] and powder X-ray diffraction methods,[15] respectively, to be $NiTi_2$-type structures,[18] but evidently the first ternary compounds with this structure type. There are three crystallographic positions in this structure: the Na atoms are on Ti(2) positions (48*f*), while the M (Au or Ag) and In atoms lie on the Ti(1) (16*c*) and Ni (32*e*) positions, respectively.

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[8] Both compounds were synthesized from stoichiometric amounts of the elements in tantalum containers which were sealed by arc-welding under argon and enclosed in an evacuated silica tube. These were allowed to react at 650 °C for 16 h before quenching, then at 300 °C for 10 days, and slowly cooled (3 °C/h) to room temperature. Both compounds have metallic luster and are air sensitive.

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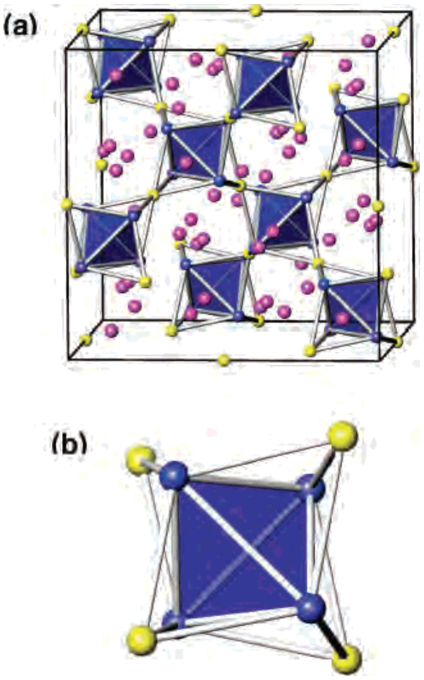

Figure 1. (a) General view of the unit cell of Na_3MIn_2; (b) tetrahedral star (TS) [$M_4Au_{4/2}$] unit. The In, M (Au or Ag), and Na atoms are colored blue, yellow, and rose, respectively.

Since X-ray diffraction cannot distinguish Ag from In well, energy dispersive electron spectroscopy (EDS) analysis of Na_3AgIn_2 yielded the ratio of Ag/In as 1.00(3):2.00(4), making their ordered dispositions reasonable. Figure 1a gives a general view of the three-dimensional framework formed by vertex-shared tetrahedral stars [$M_4Au_{4/2}$] in which the Na atoms fill the cages. A tetrahedral star is a common building block in intermetallic phases[19] and may be simply described in terms of an inner In tetrahedron that is further face-capped by Au to generate a second, larger inverted tetrahedron, the points of which are all common to neighboring units in this structure, Figure 1b. It is interesting to notice that the title compounds are also isostructural with NaBa, in which Na atoms occupy both 16*c* and 32*e* positions to form TSs, and Ba occupies the interstitial positions.[20]

Table 1. Bond Distances (Å) and −ICOHP (eV/bond) Values in Different Compounds

	Na_3AuIn_2		Na_3AgIn_2		NaIn	
bond	length	−ICOHP	length	−ICOHP	length	−ICOHP
M−In	2.927	1.423	2.960	1.219	−	−
M−Na	3.343	0.122	3.380	0.115	−	−
In−In	3.173	0.672	3.189	0.767	3.175	1.492
Na−In	3.234	0.365	3.290	0.358	3.175	0.287
Na−In	3.310	0.164	3.347	0.178	3.666	0.101

Both M and In are icosahedrally coordinated: Au is surrounded by six In and six Na atoms, while In is surrounded by three In, three Au, and six Na atoms. The Na atoms have 14 neighbors: four In, two M, and eight Na. In Na_3AuIn_2, d(In−In) = 3.173 Å is close to that in the well-known Zintl phase NaIn (d(In−In) = 3.175 Å).[21] The Na−Au distance (3.343 Å) is notably greater than d(Na−Au) = 3.13 and 3.24 Å in $Na_2Au_6In_5$[7b] and $NaAu_2$,[22] respectively. But the Na−In distances (3.233 and 3.306 Å) are shorter than d(Na−In) = 3.38−3.52 Å in $Na_2Au_6In_5$.[7b] Even shorter Na−In distances are also found in the Zintl−Klemm compound NaIn[21] (3.175 Å). Importantly, M−In and M−Na distances in the Na_3AgIn_2 compound are all little longer (~1%, 0.03−0.04 Å) than those in the Au compound, as shown in Table 1. This novelty must certainly arise from relativistic effects, which are also clearly shown in Ba_2AuTl_7.[23] Gold is famous for this,[24] and the relativistic contraction often makes the valence shell of elemental Au smaller than that of Ag. This is also shown in the molar volume difference for both compounds. The observed volume of the Au compound is 3.9% (100.4 Å^3, $Z = 16$) less than that for the Ag phase.

LMTO calculations were carried out on both compounds in order to gain some insight into the participation of sodium in the overall bonding in the structure.[25] Analyses were first done according to the calculated total densities of states (DOSs) and the separate contributions from the constituent elements (Figure 2). In terms of the projected DOS for the various atoms and their contributions to the fatbands around the Fermi level, the results for both compounds are similar. As shown in Figure 2, the states at the Fermi level, in agreement with the observed metallic properties,[28] contain

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(11) Single-crystal diffraction data for Na_3AuIn_2 were collected with the aid of Mo Kα radiation Bruker APEX SMART CCD-equipped X-ray diffractometer, from which the unique space group F*d*-3*m* (No. 227) was indicated. Absorption effects were corrected by SADABS.[12] Lattice parameters from the WinXPOW program[13] according to the positions of 37 lines from a Huber 670 Guinier powder camera data are: $a = 13.534(2)$ Å, $V = 2478.8(5)$ Å^3. The structure was solved by direct methods and refined with SHELXTL.[14] The full-matrix least-squares refinement converged at R1/wR2 [$I > 2\sigma(I)$] = 0.0146/0.0344 and R1/wR2 (all data) = 0.0148/0.0344 with 180 reflections and 11 variables (see Supporting Information).

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(15) X-ray powder data for Na_3AgIn_2 were collected on a Huber 670 Guinier powder camera as described before.[16] On the basis of the structure of Na_3AuIn_2, the Rietveld powder diffraction profile fitting technique[17] was used to get the parameters $a = 13.7140(1)$ Å, $V = 2579.25(3)$ Å^3 and to refine the structure. The latter resulted in residuals of $R_I = 0.0140$, Rp = 0.0160, and Rwp = 0.0235. The graphical comparison between the observed and calculated powder patterns, and the refinement parameters are given in the Supporting Information.

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(25) The electronic structure was calculated with the local density-functional approach and the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA) using the tight-binding program TB-LMTO-ASA.[26] The radii of the muffin-tin spheres were determined after Jepsen and Anderson.[27]

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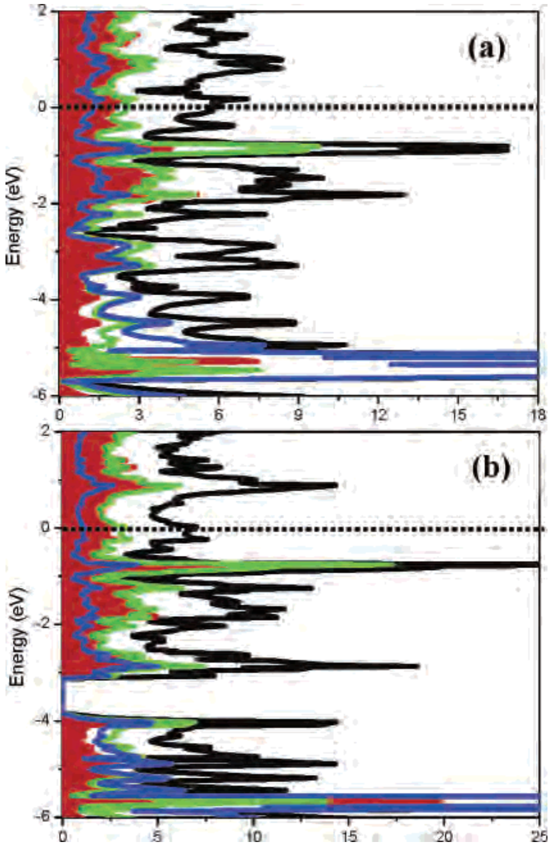

Figure 2. Densities-of-states (DOSs) (black) for (a) Na_3AuIn_2 and (b) Na_3AgIn_2. The projected partial DOS contributions of indium, gold or silver, and sodium are green, blue and red, respectively. The Na PDOS are filled in red for emphasis.

contributions from M, In, and Na. As a matter of fact, the contribution from sodium is more than 30% larger than that of M and close to that of indium. Cation mixing into M and indium states is evident. This is also reflected in the fatbands for different elements in the two compounds. Fatband plots are the band structures in which the widths of the lines are proportional to the contribution of a given set of atomic orbitals to the crystal orbitals. The fatband plots for Na s and In p orbitals in Na_3AuIn_2 in Figure 3 illustrate their significant involvement over wide energies and the important mixing of the sodium and indium orbitals. The fatbands for Au p orbitals only show small contributions at the Fermi level. There are also important cation participations below the Fermi level, as shown in Figures 2 and 3, so the cations contribute both to the bonding in and to the conductivity of the title compounds.

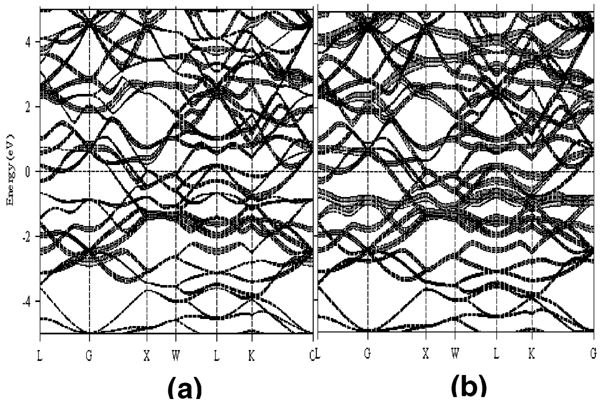

Figure 3. Energy band dispersion of Na_3AuIn_2 with fatband representations for (a) Na s and (b) In p orbitals.

To quantify the interaction between Na and In or M in the anions, the integrated crystal overlap Hamiltonian populations (−ICOHP) analyses were also determined. The −ICOHPs obtained with the first principles LMTO method are more meaningful analogues to the Mulliken overlap populations (MOPs) from extended Hückel methods and are better measures of relative bond strengths. The −ICOHP values for pairwise interactions in Na_3AuIn_2, Na_3AgIn_2, and well-known Zintl-phase NaIn[21] with the NaTl-type structure are listed in Table 1. Both M−In interactions are significantly bonding; however, those for In−In in both compounds are less than half of that in NaIn in which the In−In network is continuous. The In−In bonds in the framework in the title compounds appear to be too weak to control or dominate the overall structural stabilities, and hence, other energy terms, such as those from cation−anion interactions, also play important roles in the stabilization of the structures. This is shown here by some more interesting values for Na−In contacts. Even the longer Na−In contacts, 3.234 and 3.2902 Å, have larger −ICOHPs than the 3.175 Å contacts in NaIn. Thus, on the basis of all these observations, it can be concluded quite firmly that sodium plays an essential role in the covalent bonding of the two new structures.

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Supporting Information Available: Tables of additional crystallographic and refinement parameters for both compounds, including the graphical comparison between the observed and calculated powder pattern for Na_3AgIn_2; figures of resistivity data; and an X-ray crystallographic file for Na_3AuIn_2 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Electrical resistivities were measured by the electrodeless "Q" method with the aid of a Hewlett-Packard 4342A Q meter with 143.5 mg of powdered Na_3AuIn_2 sample.[29] The measured resistivities increase linearly over the range, and the extrapolated ρ_{298} value is about 66.2 $\mu\Omega\cdot$cm (Supporting Information).

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