Inorg. Chem. **2003**, *42*, 3988–3993

Inorganic Chemistry
Article

Quasi-1D Cations ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{n+}$ of Variable Charge: Infinite Columns ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{2+}$ in the Novel Compound $\mathrm{Ni_8Bi_8SI_2}$

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Received January 14, 2003

The new compound $\mathrm{Ni_8Bi_8SI_2}$ has been synthesized and its crystal structure determined by X-ray crystallography. The structure contains one-dimensional (1D) cations ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{2+}$ separated by iodine anions. The geometry of the columns is similar to that of the recently reported ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{+}$, and the main difference between them is only their formal charge. Electronic structure calculations and physical properties measurements were performed to analyze the influence of the number of valence electrons on the bonding and properties of compounds containing these 1D cations. It was shown that the removal of one electron (i.e., ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{+} \rightarrow {}^1_\infty[\mathrm{Ni_8Bi_8S}]^{2+}$) mainly affects the Ni–S bonding within the cation and essentially has no influence on the intermetallic Ni–Bi bonding. It was found that $\mathrm{Ni_8Bi_8SI_2}$ containing double-charged columns has conductivity properties more similar to a pure 1D metal than the congener $\mathrm{Ni_8Bi_8SI}$ containing mono-charged columns.

Introduction

Compounds containing one-dimensional (1D) isolated columns formed by condensed metal atom polyhedra represent a small but interesting family of low-dimensional compounds. Such columns can be neutral (as ${}^1_\infty[\mathrm{M_4Te_4E}]$ (M = Nb, Ta; E = Al, Si, Cr, Fe, Co, Ni) in mixed niobium or tantalum tellurides [1–3]), cationic (as ${}^1_\infty[\mathrm{Bi_{5.6}Ni_5}]^+$ in mixed nickel bismuth iodide[4] or ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^+$ in sulfoiodide[5]), or anionic (as ${}^1_\infty[\mathrm{Mo_3Ch_3}]^-$ (Ch = S, Se, or Te) in Chevrel phases [6,7]). The ability to vary the charge of such 1D columns is, in general, not known. In niobium or tantalum tellurides one obviously can change the number of valence electrons varying the E element; however, there is no information about the possibility to obtain such columns being charged. The replacement of the single-charged cation by double-charged in Chevrel phases results in drastic realignment of the structure, which becomes three-dimensional (as that of $\mathrm{BaMo_6S_8}$[8]). There is no information in the literature about the possibility to obtain other mentioned columns with the charge different from the one mentioned above.

In this work, we report the synthesis and crystal structure of the new compound $\mathrm{Ni_8Bi_8SI_2}$, which contains 1D metallic columns ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{2+}$ with the same stoichiometry and essentially the same structure but a higher formal charge as compared to the previously reported ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{+}$ columns in $\mathrm{Ni_8Bi_8SI}$. They represent the first example of the 1D columns of condensed metal polyhedra for which the charge can be varied without appreciably affecting their structure and composition. We have also investigated the electronic structure and physical properties of the new compound and compared it with those of $\mathrm{Ni_8Bi_8SI}$ to reveal the changes caused by 1D column oxidation (i.e., the increase in the column charge).

Experimental Part

Synthesis and Crystal Growth. $\mathrm{Ni_8Bi_8SI_2}$ was synthesized by annealing a stoichiometric mixture of the elements Ni (99.99,

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10.1021/ic0340332 CCC: $25.00

Table 1. Crystallographic Data for $Ni_8Bi_8SI_2$

empirical formula	$Ni_8Bi_8SI_2$
space group	*Pnnm* (No. 58)
a (Å)	9.925(2)
b (Å)	21.575(4)
c (Å)	4.158(1)
V (Å^3)	890.4(3)
Z	2
θ_{max} (deg)	21.64
μ (mm^{-1})	49.303
$R(F)$ for $F_o^2 > 4\sigma(F_o^2)^a$	0.0536
$R_w(F_o^2)^b$	0.1210

${}^{a}R(I) = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$. ^{b} $1/[\sigma^2(F_o^2) + (0.0532P)^2 + 150P]$ where $P = (F_o + 2F_c^2)/3$.

Aldrich), Bi (99.99), I_2 (99.99), and S (99.99%) in an evacuated silica ampule at 500 °C (170 h). A black solid of intergrown needle-shaped crystals with metallic luster had formed. The X-ray powder pattern (Cu Kα1 radiation, Guinier camera FR-552 [Enraf-Nonius]) showed excellent agreement with the theoretical pattern generated from the single-crystal X-ray diffraction data (see below). The substance is stable in air. For the first time, the title compound was unexpectedly obtained during the attempt to grow crystals of Ni_6BiS_3[9] by a chemical transport reaction with I_2.

To obtain suitable single crystals for physical property measurements, the sample synthesized (approximately 0.2 g) was placed in a silica tube (1.8 cm × 10 cm) together with iodine (approximately 0.02 g), and the tube was evacuated and sealed off. The growth was carried out in a horizontal gradient furnace at 500 °C (charge area) and 450 °C (at the empty end of the ampule) during 350 h. Needle-shaped dark crystals (0.01 mm × 1 mm) with metallic luster were obtained in the part of the ampule with lower temperature.

Crystal Structure Determination. A small, single crystal (0.04 mm × 0.025 mm × 0.01 mm) was mounted on a KappaCCD (Bruker-Nonius) goniometer head. Ag Kα radiation ($\lambda = 0.56090$ Å) and a graphite monochromator were used. The data sets were collected at ambient temperature. The data collection parameters and results are listed in Table 1. Semiempirical absorption correction was used. An analysis of the data collected suggested an orthorhombic crystal system with the systematic extinctions corresponding to the space group *Pnnm* (No. 58). The positions of Bi and I atoms were found using direct methods (SHELXS-97[10]). The nickel and sulfur atoms were localized by a sequence of least-squares refinement and $\Delta\rho(x,y,z)$ synthesis (SHELXL-97[10]). Finally, the positions of all atoms were refined anisotropically and the *S* site was found to be half-occupied. Because of partial *S* site occupation, single crystal and powder diffraction [Cu Kα1 radiation, Guinier camera FR-552 (Enraf-Nonius)] experiments were performed to reveal possible superstructure. However, no additional superstructure reflexes were observed on the diffraction patterns.

Measurements of Properties: (a) Thermal Properties. The substance was placed in a small quartz ampule, evacuated, and sealed off. The differential thermal analysis curve (using alumina as a standard) was recorded at a 10 °C/min heating rate on a modified PRT-1000M device equipped with a PDA-1-20 XY recorder.

(b) Resistivity. The electrical resistivity of a small crystal (needle, 0.007 mm × 0.03 mm × 1 mm) was measured parallel to the needle axis in the temperature range 4.2−300 K by employing a standard four-probe technique with the use of silver paste contacts.

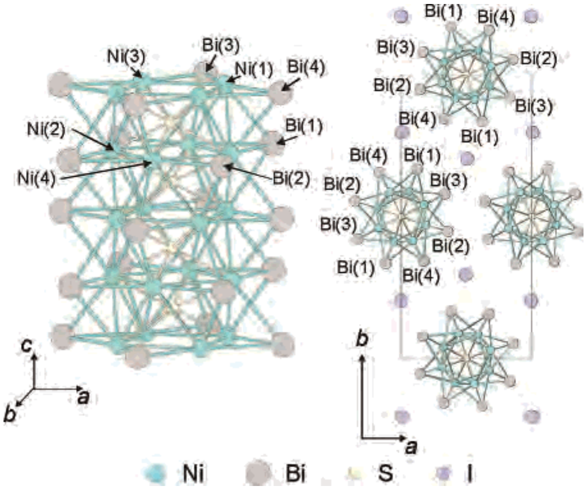

Figure 1. Crystal structure of $Ni_8Bi_8SI_2$, with the ${}^{1}_{\infty}[Ni_8Bi_8S]$ chain (left) and its packing arrangement (right).

(c) Magnetic Susceptibility. A single crystal of $Ni_8Bi_8SI_2$ (0.014 mm × 0.01 mm × 1.1 mm) was mounted on the copper holder of the original SQUID magnetometer (temperature measurement accuracy 0.2 K, sensitivity by magnetic moment 10^{-13} A/m^2 Hz$^{-1/2}$). The magnetic susceptibility was measured in the temperature range from 4.2 to 100 K in a 200 Oe magnetic field.

Calculation Details. Ab initio (RHF) and density-functional (B3LYP exchange-correlation potential) calculations were performed with the CRYSTAL98[11] program package. Hay−Wadt effective core potentials (ECPs) and basis sets,[12] which had to be modified[13] in accordance with the CRYSTAL98 manual,[11] were used in the calculations.

The analysis and visualization of difference electronic charge densities employed to reveal the nature of the bonding in $Ni_8Bi_8SI_2$ and used previously on similar compounds[5,14] were performed with the use of the TOPOND98[15] and gOpenMol[16] program packages.

Results

Crystal Structure. $Ni_8Bi_8SI_2$ is made of ${}^{1}_{\infty}[Ni_8Bi_8S]$ columns separated by iodine atoms (Figure 1). Slightly distorted square antiprisms $[Ni_8]$ share common square faces forming infinite columns running parallel along the crystallographic *c* axis. The Bi atoms reside close to the edges of each $[Ni_4]$ square. The sulfur atoms sit approximately in the centers of every $[Ni_8]$ antiprisms, but the occupation of the

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(13) Ni: An additional d-exponent of value 0.20 was added to the modified Hay−Wadt small-core basis set. Bi: The f−g term of the original ECP for Bi was eliminated. One too-diffuse exponent (<0.1) of a p-type Gaussian in the original Bi basis set was removed, and the remaining contraction was completely removed. S and I: The smallest exponents of the original basis sets for S and I were uncontracted to provide a higher degree of basis set flexibility.

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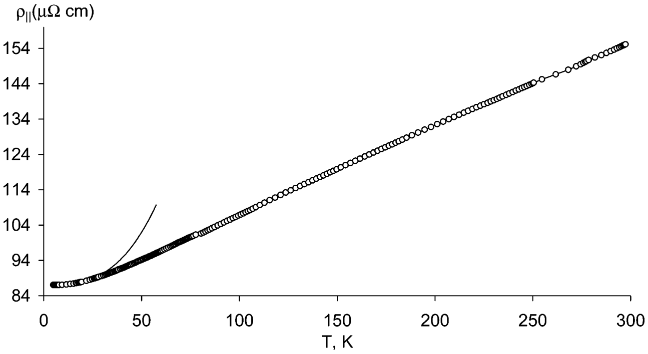

Figure 2. Resistivity of a needle-shaped crystal of $Ni_8Bi_8SI_2$. The solid line is a low-temperature fit, according to eq 1.

S site is only 1/2. These columns are packed in a close hexagonal manner (Figure 1), being separated by I atoms.

The interatomic distances within the $^1_\infty[Ni_8Bi_8S]^{2+}$ columns are close to those in Ni_8Bi_8SI. One important difference is the presence of short [2.03(4)−2.21(1) Å] distances between half-occupied sulfur positions, which are close to the typical S−S contacts in FeS_2 (2.162 Å).[17] The iodine atoms are surrounded by nine bismuth atoms with the closest Bi−I distances of 3.492(3)−3.950(2) Å. These distances are significantly longer than in mixed Ni−Bi iodides[4,18] (3.3−3.5 Å) or binary Bi iodides[19] (3.0−3.3 Å).

The "square" edges of $[Ni_8]$ antiprisms deviate by 0.07 [square formed by Ni(1) and Ni(3)] or 0.09 Å [square formed by Ni(2) and Ni(4)]. Also, the S atoms do not sit exactly in the center of the antiprism $[Ni_8]$ but are shifted about 0.04 Å along the crystallographic *c* axis, so that distances between two *S* sites in the centers of adjacent $[Ni_8]$ antiprisms become unequal (2.129 Å and 2.029 Å, respectively).

Physical Properties: (a) Thermal Properties. Four resolved endothermic effects at 454, 552, 595, and 610 °C (±5 °C) were registered in the DTA experiment (heating mode). The first effect (454 °C) should correspond to a polymorph transformation rather than decomposition because the single crystals of $Ni_8Bi_8SI_2$ in the chemical transport experiments were retrieved in the area at approximately 480 °C. The second effect (552 °C) is suggested to correspond to a solid-state decomposition because quenching from that temperature produces a nonmolten mixture of $Ni_8Bi_8SI_2$, Ni_8Bi_8SI, $Ni_3Bi_2S_2$, and probably other phases as well. Two other peaks may be attributed to the melting of the decomposition products of $Ni_8Bi_8SI_2$.

(b) Electrical Properties. The compound has a metallic type of conductivity (Figure 2). The resistivity at room temperature is equal to $\rho_{II}(300) = 160\ \mu\Omega$ cm. The temperature dependence of the resistivity $\rho_{II}(T)$ can be approximated in the range 4.2−25 K by the eq 1

$$\rho_{II}(T) = \rho_0 + kT^3 \qquad (1)$$

where $\rho_0 = 87.06\ \mu\Omega$ cm and $k = 0.00012\ \mu\Omega$ cm K^{-3}. Such dependence is characteristic of quasi-one-dimensional conductors.[20] At higher temperatures, the resistivity increases linearly up to 300 K.

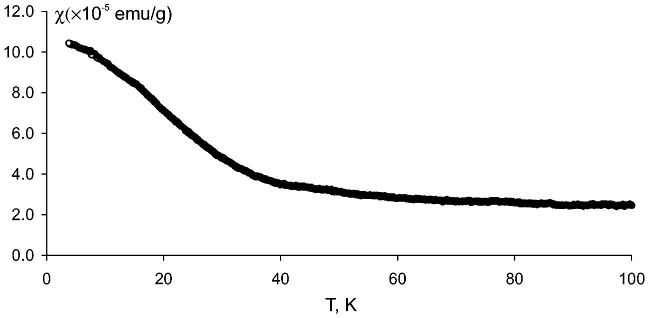

Figure 3. Temperature dependence of the magnetic susceptibility of $Ni_8Bi_8SI_2$.

Table 2. Calculated Energies (per unit cell) of Charged $^1_\infty[Ni_8Bi_8S]^{2+}$ Columns for the Different Models of S-Atom Ordering

	energy, 10^3 au
model (a) $d(S-S) = 4.158$ Å	−2.792808
model (b) $d(S-S) = 2.129$ Å	−2.792540
model (c) $d(S-S) = 2.029$ Å	−2.792584

(c) Magnetic Measurements. No magnetic anisotropy was observed. The susceptibility curve is shown in Figure 3. Such dependence is typical for temperature-independent Pauli paramagnetism of the substance with the presence of temperature-dependent Curie−Weiss paramagnetism of paramagnetic impurities (e.g., on the crystal surface). The latter is small at high temperatures ($T \approx 100$ K). The susceptibility of $Ni_8Bi_8SI_2$ was found to be $\chi(100\ K) = 2.4\ 10^{-5}$ emu/g.

Electronic Structure and Bonding. Because of the half-occupation of the *S* site in $Ni_8Bi_8SI_2$, an ordered model has to be deduced for the calculations. Apparently, the total energy depends much more strongly on the S atom arrangement within one column than on the mutual disposition of sulfur atoms belonging to different columns. It is therefore reasonable to consider different ordering arrangements of S atoms in only one column to facilitate the calculations. Three simple models were considered:

(a) S atoms regularly occupying every second $[Ni_8]$ antiprism with the S−S distance equal to 4.158 Å

(b) S atoms regularly occupying two adjacent $[Ni_8]$ antiprisms forming pairs with the S−S distance equal to 2.129 Å. The two adjacent antiprisms are, by necessity, empty to maintain the stoichiometry $^1_\infty[Ni_8Bi_8S]$.

(c) The same as (b), but the S atoms are positioned to form pairs with the S−S distance equal to 2.029 Å

The total energies of the charged columns $^1_\infty[Ni_8Bi_8S]^{2+}$ with S atoms distributed as specified in (a−c) were evaluated at HF level. The most stable ordering model was used in the calculation of the bulk $Ni_8Bi_8SI_2$ compound, for which the electronic structure and bonding were analyzed in more detail.

Table 2 presents the calculated total energies per unit cell of the $^1_\infty[Ni_8Bi_8S]^{2+}$ columns in which the S atoms are ordered as specified above. Model (a), in which the S atoms regularly occupy every second $[Ni_8]$ square antiprism and

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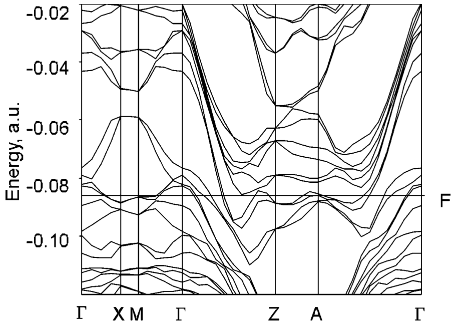

Figure 4. Band structure of $Ni_8Bi_8SI_2$.

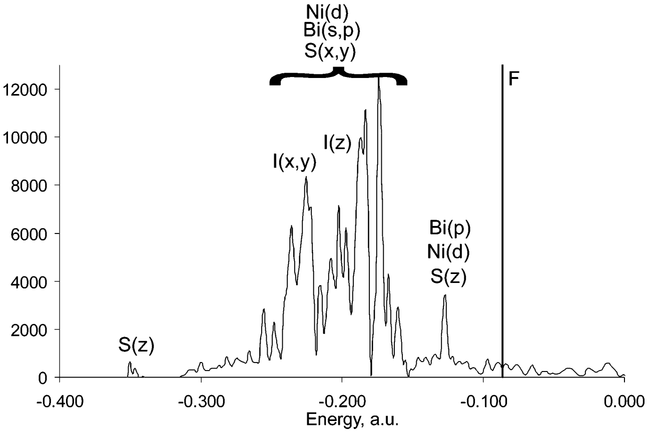

Figure 5. Total DOS of $Ni_8Bi_8SI_2$.

without direct S−S contacts [d(S−S) = 4.158 Å], was found to be the energetically most stable configuration.

In the calculations of the bulk $Ni_8Bi_8SI_2$, the unit cell dimensions were left unchanged, but because of the S-atom ordering scheme the symmetry had to be reduced from the *Pnnm* (No. 58) to the *Pnn*2 (No. 34) space group. The unit cell employed contains two independent $^{1}_{\infty}[Ni_8Bi_8S]$ columns with the S atoms arranged according to model (a). The S atoms in these columns reside at different *z/c* coordinates; thus, the columns are "shifted" by *c*/2 along the *c* axis relative to each other.

The calculated band structure and total density of states (DOS) for the whole $Ni_8Bi_8SI_2$ crystal are presented in Figures 4 and 5.

According to the band structure and DOS, $Ni_8Bi_8SI_2$ is expected to be a highly anisotropic metallic conductor. The conductivity is expected to be much higher along the *c* axis because of the number of bands that cross the Fermi level in the Γ−Z area of the Brillouin zone (i.e., the direction corresponding to the crystallographic *c* axis in real space) is much higher than that in the Γ−X−M area (i.e., corresponding to the *ab* plane in real space).

The main contributions of atomic orbitals (AOs) to the total DOS are denoted in Figure 5. Atomic states are mixed, and it is difficult to assign any of the peaks in the DOS to only one atomic state. The states in the proximity of the Fermi level have the main contribution from Bi(sp) with the admixture of Ni(d) AOs.

An analysis of partial DOS and Mulliken charges shows that the Ni atoms have almost fully occupied d-states, indicating that $Ni_8Bi_8SI_2$ should exhibit a Pauli paramagnetic behavior. The Bi s-states are fully occupied, whereas the p-states are not. The S atoms have sp-states fully occupied; a similar situation holds for iodine.

The difference charge density maps of $^{1}_{\infty}[Ni_8Bi_8S]$ are presented in Figure 6. The strongest interactions inside the columns are five-center heterometallic interactions 4Ni + Bi (marked as A) and 4Bi + Ni (marked as B). Intermetallic interaction is often of multicenter nature as reported earlier for metals,[21] intermetallics,[14] and the analogous compound Ni_8Bi_8SI.[5] The interaction between nickel and sulfur is also not pairwise and corresponds to five-center 4Ni + S, marked as *C* (Figure 7). The shape and positions of these *C* maxima imply that the S $3p_z$ states are one of the major contributors to these interactions, and indeed, $3p_z$ states of S give a pronounced peak on the DOS curve at −0.13 au (Figure 5).

The interaction between the infinite $^{1}_{\infty}[Ni_8Bi_8S]$ column and iodine are of almost purely electrostatic nature, as can be observed from the spherical isosurface close to the iodide ion (Figure 8). The calculated formal (Mulliken) charge on iodine is close to −1. Together with the long Bi−I contacts, this supports the interpretation of the columns as $^{1}_{\infty}[Ni_8Bi_8S]^{2+}$.

Discussion

The crystal structure of $Ni_8Bi_8SI_2$ is highly related to that of the previously reported Ni_8Bi_8SI,[5] which also contains 1D columns of $^{1}_{\infty}[Ni_8Bi_8S]$ packed parallel to each other and separated by iodine anions. The increase in column charge and thus required doubling of the amount of iodine introduces some changes in the crystal and electronic structure as compared to Ni_8Bi_8SI.

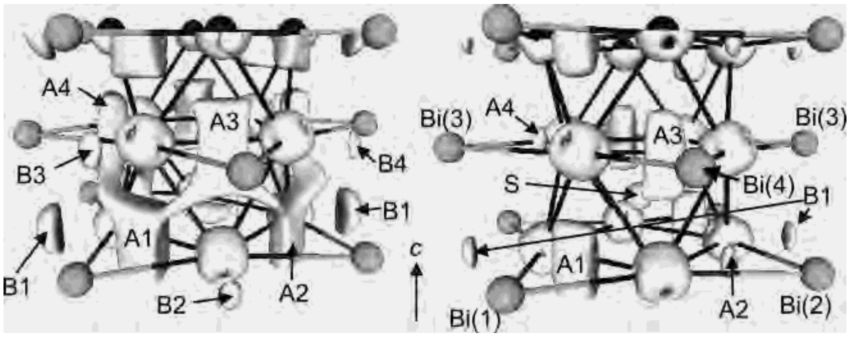

Figure 6. Difference charge density distribution in the $^{1}_{\infty}[Ni_8Bi_8S]$ column. $\Delta\rho = +0.0145$ e$^-$ au^{-3} (left) and $\Delta\rho = +0.018$ e$^-$ au^{-3} (right).

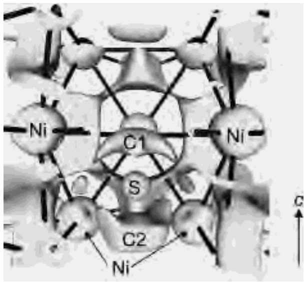

Figure 7. Difference charge density inside the ${}^1_\infty[\mathrm{Ni_8Bi_8S}]$ column around the S atom. $\Delta\rho = +0.013$ e^- au^{-3}.

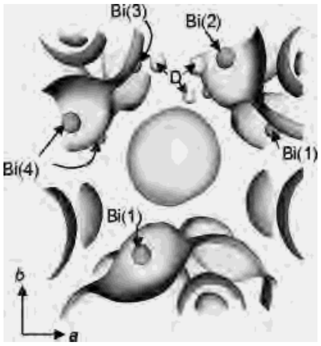

Figure 8. Difference charge density close to I^-. $\Delta\rho = +0.002$ e^- au^{-3} (isosurface of close-to-almost-spherical shape hides the I^- anion inside it). D stands for Bi lone-pairs.

The columns in $\mathrm{Ni_8Bi_8SI}$ are packed in a square motif, whereas in $\mathrm{Ni_8Bi_8SI_2}$ they are packed in a hexagonal array. This can be attributed to the increased number of separating anions and to an increase in the charge of the columns leading to stronger electrostatic interaction and closer packing. In coherence, the shortest Bi−I separations in $\mathrm{Ni_8Bi_8SI_2}$ (3.492 Å) are shorter than in $\mathrm{Ni_8Bi_8SI}$ (3.930 Å).[5]

Another difference between the crystal structures of $\mathrm{Ni_8Bi_8SI}$ and $\mathrm{Ni_8Bi_8SI_2}$ is the statistical distribution of sulfur atoms in the latter. According to calculation results, the energetically most stable model of sulfur distribution in the columns of $[\mathrm{Ni_8}]$ antiprisms is the occupation of every second antiprism in a regular order, just as in $\mathrm{Ni_8Bi_8SI}$. Therefore, it is logical to assume that the sulfur atoms in the ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{2+}$ columns of the $\mathrm{Ni_8Bi_8SI_2}$ structure are regularly distributed, but the columns are packed with a statistical shift along the *c* axis, giving rise to the half-occupied sulfur positions.

The removal of one electron per formula unit in ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{2+}$, as compared to ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{+}$, essentially changes the nature of the nickel−sulfur interaction in the columns from classical pairwise to a multicenter type because of the deficiency of electrons. The positions of these two 4Ni + S maxima (above and below S along the *z* coordinate) imply that the S $3p_z$ orbitals are involved in this interaction to a greater extent than other S 3p states. Hence, the S $3p_z$ orbitals have a different energy because of that interaction that resulted in the pronounced peak on the DOS curve. In contrast, eight Ni−S maxima in $\mathrm{Ni_8Bi_8SI}$ are located in the corners of the distorted cube that requires all S 3p-states to be almost equally mixed in this interaction.

It is worth noting that this "oxidation" does not seriously affect the heterometallic bonds. However, the shortest interatomic distances within the columns in $\mathrm{Ni_8Bi_8SI_2}$ {e.g., $d[\mathrm{Ni(2)-Bi(1)}] = 2.705(4)$ Å, $d[\mathrm{Ni(1)-Ni(2)}] = 2.555(3)$ Å} are longer than the shortest contacts in $\mathrm{Ni_8Bi_8SI}$ [$d(\mathrm{Ni-Bi}) = 2.679(1)$ Å, $d(\mathrm{Ni-Ni}) = 2.519(1)$ Å]. Probably the "oxidation" reduces the overall electronic density in the bonding regions, or alternatively expressed, removes the electrons from bonding states weakening the bonding observed as an increase in atom−atom distances.

The results of the physical measurements show $\mathrm{Ni_8Bi_8SI_2}$ to be a quasi-one-dimensional metallic conductor exhibiting Pauli paramagnetism. These results are in good agreement with those of the quantum-chemical calculations performed. Similar properties were reported earlier for $\mathrm{Ni_8Bi_8SI}$.[5] However, a comparison of the low-temperature resistivity dependencies of the two compounds shows that the low-temperature power law deviates from the experimental data at different temperatures: at 25 K for $\mathrm{Ni_8Bi_8SI_2}$ and at 45 K for $\mathrm{Ni_8Bi_8SI}$. This deviation temperature T_d is associated with the amplitude of the goffer of the Fermi surface[20] γ ($\gamma \approx T_d$), which in turn can be considered as a measure of the interaction between the 1D systems, i.e., the columns ${}^1_\infty[\mathrm{Ni_8Bi_8S}]$. Consequently, the amplitude of the goffer of the Fermi surface in $\mathrm{Ni_8Bi_8SI_2}$ is lower than in $\mathrm{Ni_8Bi_8SI}$, and the interaction between the 1D columns in the former compound is thus less pronounced. This can be attributed to the double amount of iodine, which acts as an insulating matrix between the cationic columns.

One-dimensional columns of condensed metal polyhedra may demonstrate surprising structural stability, viz. the niobium or tantalum tellurides. They allow the replacement of niobium by tantalum and they vary the E element from Al or Si to Cr−Ni, indicating a significant electron-buffering capacity of the columns. The only possible element change in Chevrel phases is the replacement of S by Se or Te, thus conserving the number of valence electrons. The electron-buffering capacity of the cationic ${}^1_\infty[\mathrm{Ni_8Bi_8S}]$ columns, indicated by the possibility of changing their formal charge, may suggest that the number of valence electrons can be varied not only via the total column charge but also by heterovalent substitution of the elements of the column core. Several attempts to expand the series of such 1D compounds with heterometallic columns by metal substitutions have been initiated. The samples of the compositions T:M:S:I = 8:8:1:1 and 8:8:1:2 (where T = Fe, Co, Ni; M = Sn, Pb, Sb, Bi), derived by complete substitution of only one metallic core element by another in $\mathrm{Ni_8Bi_8SI}$ and $\mathrm{Ni_8Bi_8SI_2}$, were studied under similar conditions (evacuated silica ampules, 500−540 °C). Attempts have also been made to synthesize the derivative compound $\mathrm{Ni_8Bi_8SI_{3/2}}$, potentially with both types of columns (${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{+}$ and ${}^1_\infty[\mathrm{Ni_8Bi_8S}]^{2+}$). However, none of those attempts have yet been successful. X-ray phase analysis of the samples synthesized revealed no new low-dimensional phase similar to $\mathrm{Ni_8Bi_8SI}$ or $\mathrm{Ni_8Bi_8SI_2}$. Only a mixture of the elements, known binary or ternary compounds, were discovered in the ampules. The sample with the

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(21) Silvi, B.; Gatti, C. *J. Phys. Chem. A* **2000**, *104*, 947.

composition $Ni_8Bi_8SI_{3/2}$ was found to be a mixture of Ni_8Bi_8SI and $Ni_8Bi_8SI_2$.

It is highly likely that the heterovalent substitutions attempted above (i.e., Ni → Co, Fe; Bi → Sn, Pb) lead to a significant deficiency of valence electrons affecting the column stability. One can expect that homovalent substitutions (Bi → Sb, Ni → Pd, Pt) could be more likely to render success, although geometric factors should not be forgotten; the radii of the substituents may differ too much to allow replacement without collapse of the 1D structure building blocks.

Conclusions

$^{1}_{\infty}[Ni_8Bi_8S]^{n+}$ cations existing in mixed nickel−bismuth sulfoiodides present an interesting case of 1D objects whose charge can be varied without seriously affecting their structure and composition. To our knowledge, this is the first example of 1D systems of variable charge composed of condensed metal polyhedra. Electronic structure calculations showed that only some kinds of bonds (Ni−S) are affected by electron removal, being transformed from pairwise to multicenter, whereas others (intermetallic Ni−Ni and Ni−Bi) are not. Probably this is the reason these columns allow removal or addition of one electron and can have both a +1 and +2 formal charge.

Compounds containing $^{1}_{\infty}[Ni_8Bi_8S]^{n+}$ demonstrate similar physical properties (1D conductivity, Pauli paramagnetism) attributed to the presence of the columns with a metallic core separated by iodine in their structures. An increase in the column charge and doubling of the amount of iodine in $Ni_8Bi_8SI_2$ results in enhanced 1D conductivity as compared to Ni_8Bi_8SI.

Acknowledgment. We thank Salavat M. Ishikaev for the measurements of the physical properties. This work was supported by INTAS program (Grant No. 99-1672) and the Russian Foundation for Basic Research (Grant No. 00-03-32647a).

Supporting Information Available: X-ray crystallographic file for $Ni_8Bi_8SI_2$ (CIF) and basis sets and ECPs used in calculations (input cards for CRYSTAL98, text). These materials are available free of charge via the Internet at http://pubs.acs.org.

IC0340332