New polymolecular bismuth monohalides. Synthesis and crystal structures of $Bi_4Br_xI_{4-x}$ (x = 1, 2, or 3)

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New mixed bismuth monohalides $Bi_4Br_xI_{4-x}$ (x = 1, 2, or 3) were prepared for the first time by the reactions of bismuth metal with bismuth trihalides taken in stoichiometric amounts. Their crystal structures were established by single-crystal X-ray diffraction analysis. The Bi_4Br_3I and Bi_4BrI_3 compounds are isostructural and crystallize in the orthorhombic system, and $Bi_4Br_2I_2$ crystallizes in the monoclinic system. The crystal structures of all three phases contain one-dimensionally infinite molecular chains consisting of the $[Bi_4X_4]$ fragments whose structures are identical with those of the individual Bi_4I_4 and Bi_4Br_4 molecules. The molecules are packed in layers. Different packing modes of the layers were found for different bismuth monohalides. The Bi_4ClI_3 compound, which is apparently structurally similar to Bi_4Br_3I and Bi_4BrI_3, was also prepared.

Key words: bismuth monohalides, infinite clusters, X-ray diffraction analysis.

Two types of crystalline compounds containing infinite bismuth clusters are known. One type involves chalcogenides Bi_4Z_3 and Bi_2Z_2 (Z = Se or Te).[1,2] In the structures of these compounds, the corrugated layers of Bi atoms alternate with the tetradymite-like Bi—Z layers along the axis *c* of hexagonal unit cells. Another type of compounds comprises monohalides Bi_4X_4 (X = Br or I)[3–5] and subiodidies $Bi_{14}I_4$ [6] and $Bi_{18}I_4$.[7] The structures of these halides are built of polymeric molecules, each being a one-dimensionally infinite fragment of the structure of bismuth metal varying in width (4, 14, or 18 Bi atoms). Such structures are formed only with bromine and iodine, whereas the only known low-valent bismuth chloride, *viz.*, $Bi_{12}Cl_{14}$ [8,9] (isostructural to $Bi_{12}Br_{14}$[3]), contains the ligand-free Bi_9^{5+} cations.

In the present study, we synthesized mixed bismuth monohalides $Bi_4X_xX'_{4-x}$ (X and X′ = Cl, Br, or I; x = 1, 2, or 3) and established their crystal structures. The solid-phase reactions in the Bi_4I_4—Bi_4Br_4, Bi_4I_4—"Bi_4Cl_4", and Bi_4Br_4—"Bi_4Cl_4" systems were examined by the ampule method. Selected preliminary results have been published previously.[10] In the present study, we report the complete data and analyzed the characteristic features of the crystal structures of the bismuth monohalides.

Results and Discussion

Investigation of the solid-phase reactions in various systems gave the following results.

The Bi_4I_4—Bi_4Br_4 system. Three new phases, *viz.*, Bi_4Br_3I (I), $Bi_4Br_2I_2$ (II), and Bi_4BrI_3 (III), were found. All phases were obtained as air- and moisture-stable black polycrystalline powders. All lines in the Guinier powder patters of phases I and III were indexed in the orthorhombic system, and the lines for phase II were indexed in the monoclinic system. The specimens whose compositions were intermediate between those mentioned above were mixtures of two adjacent phases. Impurities of the adjacent phases were observed even in specimens, which differed in composition from one of the individual phases by only 2 mol.%. No changes in the unit cell parameters were revealed based on the X-ray diffraction patterns of the specimens in the two-phase regions. Hence, the Bi_4I_4—Bi_4Br_4 system is quasibinary and the homogeneity regions of the phases found are narrow. Within the accuracy of powder X-ray diffraction analysis, the widths of these homogeneity regions can be estimated as at most 2 mol.%.

The Bi_4I_4—"Bi_4Cl_4" system. In this system, only one new phase (IV) was found. Its composition is close to Bi_4ClI_3, and its X-ray pattern was indexed in the orthorhombic system. The Guinier powder pattern of an annealed specimen, which precisely corresponds in composition to Bi_4ClI_3, has additional weak reflections of $Bi_{12}Cl_{14}$. According to the powder X-ray diffraction data, the specimen of composition $Bi_4Cl_{0.5}I_{3.5}$ was a mixture of phase IV and Bi_4I_4, the unit cell parameters of phase IV remaining unchanged. The same phase with the identical unit cell parameters was found in speci-

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Table 1. Crystallographic data and details of X-ray diffraction analysis of $Bi_4Br_{4-x}I_x$ (x = 1, 2, or 3)

Parameter	Bi_4Br_3I	$Bi_4Br_2I_2$	Bi_4BrI_3
Symmetry	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Cmc2_1$	$C2/m$	$Cmc2_1$
a/Å	4.3558(5)	13.617(2)	4.382(1)
b/Å	13.453(2)	4.3795(7)	13.993(3)
c/Å	19.327(2)	29.507(5)	19.636(5)
β/deg	—	96.72(1)	—
V/Å^3	1132.5(4)	1747.6(9)	1204.0(8)
Z	4	6	4
ρ_{calc}/g cm^{-1}	7.052(3)	7.123(4)	7.152(6)
Crystal dimensions/mm	0.11×0.10×0.10	0.25×0.06×0.04	0.20×0.06×0.05
μ/cm^{-1}	728.05	698.20	666.41
$(\sin\theta/\lambda)_{max}$	0.615	0.594	0.659
Number of independent reflections	654	1757	842
Number of reflections used in the refinement	435	791	497
Criterion used in the refinement	$6\sigma(F_0)$	$4\sigma(F_0)$	$6\sigma(F_0)$
Number of refinable parameters	48	74	48
R	0.056	0.047	0.055
R_w	0.062	0.053	0.055
Programs used for calculations	SDP[11]	SDP	CSD[12]

mens enriched with "Bi_4Cl_4", which contained also $Bi_{12}Cl_{14}$ and bismuth metal.

In the Bi_4Br_4—"Bi_4Cl_4" system, no new phases were detected. All specimens were compoosed only of bismuth metal, $Bi_{12}Cl_{14}$, and $Bi_{12}Br_{14}$.

Crystal structures. The powder X-ray diffraction patterns of all mixed bismuth monohalides under study indicated that the structures of these phases differred from those of Bi_4I_4 and Bi_4Br_4. At the same time, phases I and III give similar X-ray patterns, which differ only by a systematic shift of the reflection positions. This is evidence that the latter phases are isostructural. The crystal structures of phases I, II, and III were established by single-crystal X-ray diffraction analysis. The crystallographic data and details of X-ray diffraction analysis for three compounds are given in Table 1.

Analysis of the initial data set for Bi_4BrI_3 confirmed the orthorhombic symmetry. The systematic absences (hkl: $h + k \neq 2n$, $h0l$: $l \neq 2n$) indicated three possible space groups, *viz.*, $Cmc2_1$, $Ama2$, and $Cmcm$. The refinement demonstrated that the space group $Cmc2_1$ is most reliable. All atoms (4 Bi + 4 X) were revealed by direct methods. The occupancies of the positions of the halogen atoms were refined, which gave 75% of I and 25% of Br for all four atomic positions. These values were fixed in accordance with the composition Bi_4BrI_3 and the isotropic refinement by the least-squares method converged to $R = 0.063$ for 497 independent reflections with $F_0 > 6\sigma(F_0)$. The final anisotropic refinement with fixed occupancies for the positions of the halogen atoms reduced the R factor to 0.055. In the difference Fourier map, the chemically significant peaks were absent.

Since it was established that the Bi_4Br_3I phase is isostructural to the phase described above, we refined it according to the same procedure. All positions of the halogen atoms were occupied by the I and Br atoms by 25% and 75%, respectively. The final difference Fourier map contained no chemically significant peaks.

The initial data set for a specimen of $Bi_4Br_2I_2$ confirmed the monoclinic system. The systematic absences indicated the space groups $C2$, Cm, or $C2/m$. The positions of six Bi atoms and four halogen atoms were revealed from the three-dimensional Patterson function, which demonstrated that all these atoms occupy the special positions (x, 0, z). The positions of the remaining atoms were located by performing the least-squares cycles of the refinement alternated with calculations of Fourier maps within the space group $C2/m$. The occupancies of the positions of the halogen atoms were refined to give 75% of I and 25% of Br for one atomic position, 25% of I and 75% of Br for another position, and 50% of I and 50% of Br for the remaining four positions. The occupancies were determined in accordance with the composition $Bi_4Br_2I_2$. The structure was refined isotropically to $R = 0.076$ for 791 reflections with $F_0 > 4\sigma(F_0)$. Finally, the structure was refined anisotropically. The final difference Fourier map contained no chemically significant peaks. The refinement in the noncentrosymmetrical space group Cm (all positions of the type x, 0, z) gave less accurate results and did not allow us to reveal the superstructure associated with the possible different occupancies of the positions of the halogen atoms.

The principal interatomic distances and angles in the crystal structures of bismuth monohalides (both of those established in the present study and those reported previously) are given in Table 2.

We failed to obtain single crystals of phase IV suitable for X-ray diffraction studies. However, the similarity of the powder X-ray diffraction patterns of phases I,

Table 2. Principal interatomic distances and angles in the structures of bismuth monohalides

Phase	Distance/Å			Angle/deg		Reference
	Bi_{in}—Bi_{in} (×2)	Bi_{in}—Bi_{ex} (×1)	Bi_{ex}—X (×4)	Bi—Bi_{in}—Bi (×3)	X—Bi_{ex}—X (×4)	
Bi_4Br_4	3.02	3.04	2.94—2.95	89.5—91.8	92.4—95.1	3
Bi_4Br_3I	3.02	3.04—3.05	2.98—3.03	91.6—92.3	86.3—94.0	This study
$Bi_4Br_2I_2$	3.02—3.03	3.05	3.01—3.10	91.5—92.9	87.0—93.2	This study
Bi_4BrI_3	3.02	3.04—3.05	3.07—3.11	92.2—93.2	88.6—91.1	This study
α-Bi_4I_4	3.04	3.04—3.06	3.11—3.16	92.4—93.5	89.1—90.8	4
β-Bi_4I_4	3.04	3.07	3.13—3.14	92.1—93.6	89.7—90.0	4

III, and IV suggests that phase IV is isostructural to phases I and III. Indexing of the powder X-ray diffraction pattern for phase IV gave the following unit cell parameters: $a = 4.414(1)$, $b = 14.264(4)$, $c = 19.868(5)$ Å.

The projections of the crystal structures of phases I and II onto the planes (100) and (010), respectively, are shown in Figs. 1 and 2. The crystal structures of all compounds under consideration as well as of Bi_4I_4 (both of the α and β forms) and Bi_4Br_4 are based on the same primary "building block", *viz.*, on the one-dimensionally infinite ${}^{1}_{\infty}(\mathrm{Bi_4X}_x\mathrm{X'}_{4-x})$ molecule, which is four Bi atoms wide (Fig. 3). The Bi atoms in the molecule can be divided into two types. Each "internal" Bi atom (Bi_{in}) is surrounded by three nearest neighboring Bi atoms at distances of 3.02—3.04 Å (analogously to the structure of bismuth metal) and one halogen atom located at a larger distance (3.6—3.7 Å). Each "external" Bi atom (Bi_{ex}) is bound to one "internal" Bi atom and four halogen atoms, d(Bi—X) = 2.94—3.16 Å. The molecule has the symmetry axis 2_1, which hereinafter will be referred to as the molecular axis. In the structures of all bismuth monohalides, the corresponding molecular translation is ~4.2 Å.

In the crystal structures, the molecules form the ${}^{2}_{\infty}(\mathrm{Bi_4X}_x\mathrm{X'}_{4-x})$ layers (Fig. 4, *a*) within which the molecular axes are parallel to each other and lie in a single plane ("the layer plane"). In each layer, the adjacent molecules are shifted with respect to each other by one-half the molecular translation. The arrangement of the molecules within each layer provides additional coordination of all Bi_{in} atoms by two halogen atoms belonging to one of the adjacent molecules, d(Bi—X) = 3.6—3.9 Å (Fig. 4, *b*). Hence, taking into account one halogen atom from its own layer, the coordination of the Bi_{in} atom in the monohalides, like that of the bismuth atom in the structure of bismuth metal, is 3 + 3.

In the structures of all bismuth halides, the ${}^{2}_{\infty}(\mathrm{Bi_4X}_x\mathrm{X'}_{4-x})$ layers have the same geometry and differ

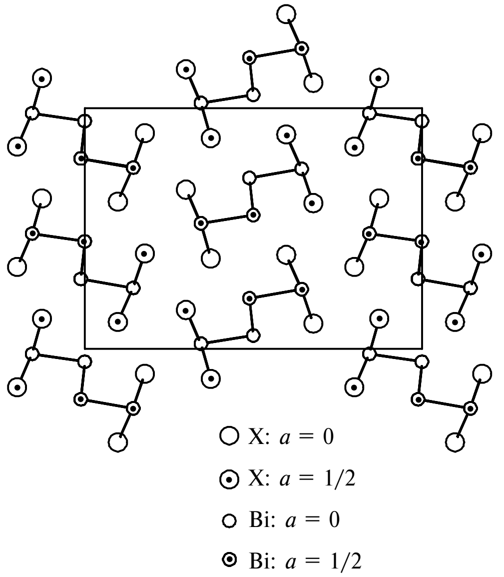

Fig. 1. Crystal structure of Bi_4BrI_3 projected onto the plane (100).

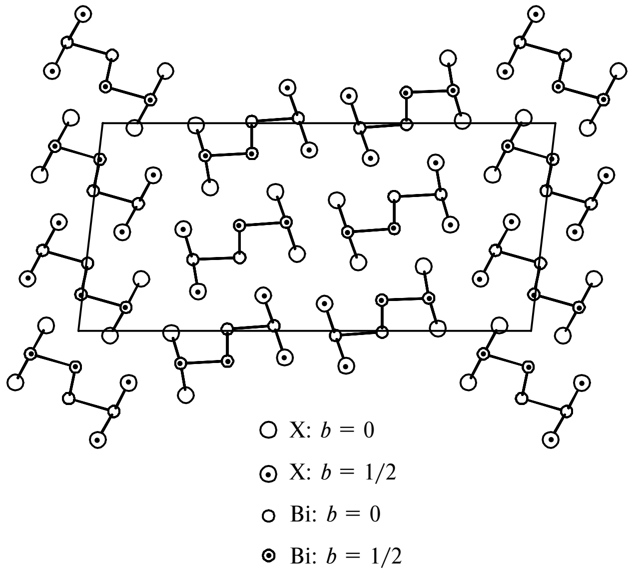

Fig. 2. Crystal structure of $BiBr_2I_2$ projected onto the plane (010).

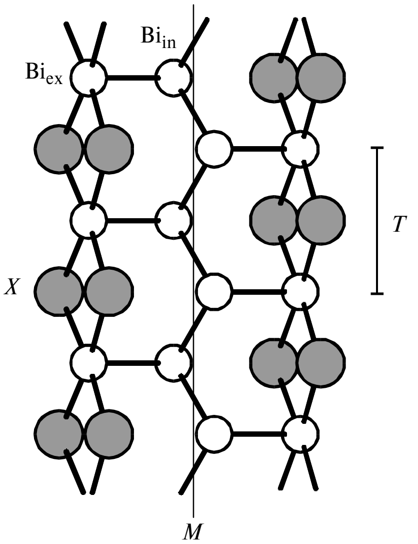

Fig. 3. Overall view of the $^1_\infty[Bi_4X_4]$ molecules in the crystal structures of $Bi_4Br_{4-x}I_x$ (*M* is the molecular axis and *T* is the translation).

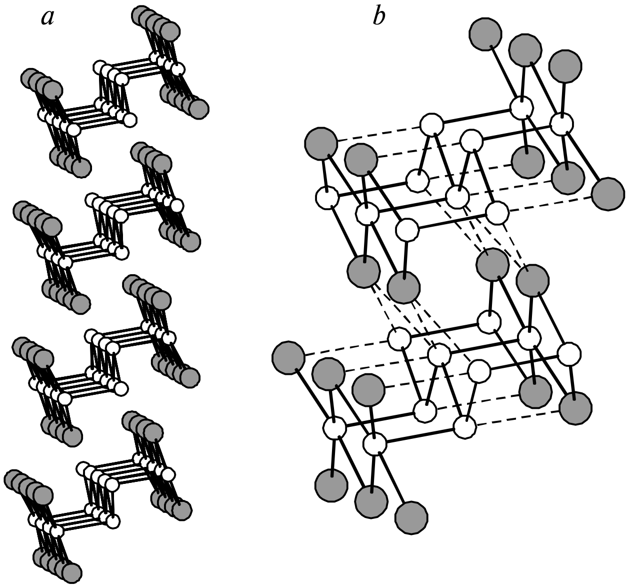

Fig. 4. Fragment of the $^1\infty[Bi_4X_4]$ layer in the structures of $Bi_4Br_{4-x}I_x$ (*a*); the modes of coordination of the atoms of two adjacent molecules in the layer (*b*); the short Bi—Bi and Bi—X distances are indicated by solid lines and the larger Bi—X distances (3.6—3.9 Å) are shown by dashed lines.

only by the nature of the halogen atoms in the corresponding positions. However, the layers in the structures are arranged in different fashions. Two types of these layers can be distinguished. The layers of different types are related to one another by the mirror reflection in the layer plane. In any case, the direction of the layer packing coincides with the axis *c* of the unit cell, and the planes of all layers are parallel to each other. In the structures of phases I and III (see Fig. 1) and Bi_4Br_4

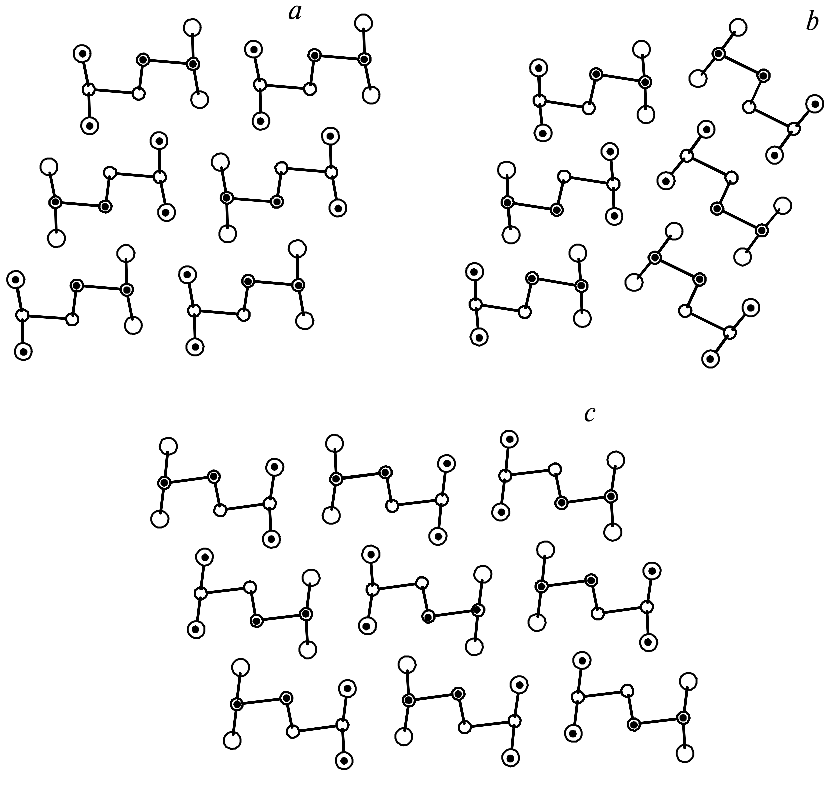

Fig. 5. Crystal structures of β-Bi_4I_4 (*a*), Bi_4Br_4 (*b*), and α-Bi_4I_4 (*c*) projected along the corresponding molecular axes. The atomic numbering schemes are given in Fig. 1.

(Fig. 5, *c*), the mirror-reflected layers alternate with each other. In the structure of phase II, the layers are packed in a more complex way, *viz.*, two "normal" layers alternate with one mirror-reflected layer (see Fig. 2). At the same time, the structures of both modifications of Bi_4I_4 are built of the layers of only one type[4] (Fig. 5, *a*, *c*).

In addition, two modes of packing of the identical layers are observed in the structures under consideration. In the structure of β-Bi_4I_4, each Bi_{ex} atom is additionally coordinated by one I atom from the adjacent layer, d(Bi—I) = 3.8 Å (see Fig. 5, *a*). Another packing mode of the layers is observed in the crystals of α-Bi_4I_4 in which the coordination of each Bi_{ex} atom is completed with two I atoms from the adjacent layer, d(Bi—I) = 4.2 Å (see Fig. 5, *c*). In the structure of α-Bi_4I_4, alternation of both packing modes is observed. It is readily seen that one mode of packing of the layers can be obtained from another one by shifting one of the adjacent layers by one-half the molecular translation.

The structure of Bi_4Br_4, like those of phases I and III, is characterized only by one mode of the combined packing of the "normal" and mirror-reflected layers, which differs from those described above. In the structures of the latter compounds, the Bi_{ex} atoms belonging to different stacking layers differ in the coordination mode. Thus, all Bi_{ex} atoms of one layer are additionally coordinated by two halogen atoms from another layer, d(Bi—X) = 3.9—4.0 Å, whereas all Bi_{ex} atoms from the adjacent layer have only one "extraneous" halogen atom as the nearest neighbor at the same interface, d(Bi—X) = 3.5—3.8 Å (see Fig. 5, *b*). The structure of phase II can be described as alternation of different modes of packing characteristic of α-Bi_4I_4 and Bi_4Br_4.

In the structures of all known bismuth monohalides, two parameters of the unit cells are approximately equal regardless of the chemical composition. These parameters correspond to two mutually perpendicular crystallographic axes. One of these parameters is the above-described molecular translation (4.2 Å). Another parameter characterizes the translation within the layer.

The direction of the third crystallographic axis always coincides with the direction along which the layers are packed. Depending on the nature of the halogen atom as well as on the type of the layers and the mode of their packing, the phase belongs to either the orthorhombic system (phases I and III) or the monoclinic system (α- and β-Bi_4I_4, Bi_4Br_4, and phase II) as dictated by the corresponding translation. Evidently, the value of the latter parameter depends on the number of layers per unit cell and is approximately equal to 10 Å. The unit cell parameters of all known bismuth monohalides are listed in Table 3.

Apparently, the energies of the packing modes should differ only slightly and new (presently unknown) modes of alternation of the layers in polytypes of bismuth monohalides would be expected to exist. This assumption is confirmed, for example, by the preparation[4] of the γ modification of Bi_4I_4 (however, its structure has not been established). In addition, we have observed[13] the phase transition in the Bi_4I_4 compound at 15 °C.

Table 3. Unit cell parameters of bismuth monohalides

Phase	Space group	*a*	*b*	*c*	β/deg	Reference
		Å				
Bi_4Br_4	*C*2/*m*	13.064	4.338	20.061	107.42	3
Bi_4Br_3I	*Cmc*2_1	4.356	13.453	19.327	—	*
$Bi_4Br_2I_2$	*C*2/*m*	13.617	4.380	29.507	96.72	*
Bi_4BrI_3	*Cmc*2_1	4.382	13.993	19.636	—	*
α-Bi_4I_4	*C*2/*m*	14.245	4.428	19.968	92.96	4
β-Bi_4I_4	*C*2/*m*	14.376	4.430	10.493	107.87	4

* This study.

Experimental

Bismuth of high purity grade (>99.999%) was used as the starting reagent. Bismuth trihalides were synthesized from the corresponding elements and purified by sublimation according to a procedure described previously.[5,7] The compositions of the specimens in the Bi_4I_4—Bi_4Br_4, Bi_4I_4—"Bi_4Cl_4", and Bi_4Br_4—"Bi_4Cl_4" systems were initially measured with a step of 25 mol.%. At the next stage, the compositions, which were close to those of the compounds found, were examined with a step of 2 mol.%. In all cases, bismuth trihalides and bismuth metal were mixed and ground in a dry chamber; the total weight of the specimens was *c.a.* 0.5 g. The resulting mixtures were placed in quartz ampules, which were sealed *in vacuo* and annealed at 260 °C for 20—30 days. The phase compositions of the annealed specimens and the attainment of the equilibrium state in these specimens were monitored by powder X-ray diffraction analysis using the Guinier method (a Nonius FR-552 chamber, Cu-Kα_1 radiation, a Ge powder as the internal standard).

Crystals were prepared from melts and the gas phase according to procedures, which have been used previously for the preparation of single crystals of bismuth subiodides (the method was described in detail in Ref. 14). Only twins were obtained by growing from the gas phase, whereas the crystals of phases I, II, and III suitable for X-ray diffraction analysis were obtained from the melts. Attempts to prepare crystals of phase IV suitable for X-ray studies failed.

X-ray diffraction study. In all cases, the single-crystal character of the specimens was confirmed by recording Laue patterns. The crystals of phases I, II, and III were glued to Pyrex-glass whiskers. X-ray diffraction studies were carried out on a Nonius CAD-4 diffractometer (Mo-Kα radiation, λ = 0.71073 Å). The unit cell parameters were refined using 24 well-centered reflections in the angle range $15° < \theta < 18°$. The intensity data were collected at ~20 °C. The corrections for the Lorentz and polarization factors were applied automatically. Because of the irregular shape of the crystals used, the numerical absorption correction was not employed; instead, the semiempirical absorption correction was applied using the azimuth scanning technique. The detailed information on the crystal structure determination can be obtained from the authors or ordered from FACHINFORMATIONSZENTRUM KARLSRUHE, D-76344 Eggenstein-Leopoldshafen (Germany) using either the deposit numbers CSD-410594, CSD-410613, and CSD-410614 or the names of the authors.

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