

Two New Cubic Structures of Mercury Arsenidehalides

Andrei V. Shevelkov, Evgeny V. Dikarev,¹ and Boris A. Popovkin

Department of Chemistry, Moscow State University, Moscow 119899, Russia

Received April 1, 1996; in revised form July 29, 1996; accepted August 1, 1996

Crystal structures of $\text{Hg}_4\text{As}_2\text{Br}_3$ (I) and $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$ (II), which was prepared for the first time, have been refined based on the X-ray single crystal experiments. Both phases crystallize in the cubic space group $Pa\bar{3}$. Crystal data: I, $a = 12.610(1)$, $Z = 8$, $R_1 = 0.0602$; II, $a = 12.178(1)$, $Z = 4$, $R_1 = 0.0584$. Characteristic of both structures are the As_2Hg_6 octahedra having an As–As separation of ca. 2.38 Å. Such octahedra share vertices with AsHg_4 tetrahedra in I, while in II they compose a perovskite-like three-dimensional network by sharing all vertices. Part of the mercury atoms in II have no neighbors up to 3.53 Å and are considered to possess a zero oxidation state. An idealized path for the I to II structure transformation, which is based on the difference of halogen radii, is suggested. © 1996 Academic Press, Inc.

INTRODUCTION

A large family of mercury and cadmium pnictidohalides has been discovered since the beginning of the 1960s. Of the more than 40 ternary and quaternary phases (1), almost one half possess either $M_4Z_2X_3$ or $M_7Z_4X_6$ ($M = \text{Cd}, \text{Hg}$; $Z = \text{P}, \text{As}, \text{Sb}$; $X = \text{Cl}, \text{Br}, \text{I}$) stoichiometry. The two stoichiometries differ slightly by metal content, and while the 7:4:6 phases contain Z_2^{4-} dumbbells, in the 4:2:3 phases such dumbbells alternate with Z^{3-} anions. Despite having both different composition and pnictide anions of a different nature, all these phases have similar crystal structures: (i) they crystallize in the cubic space group $Pa\bar{3}$ with the unit cell parameter a close to 12 Å; (ii) their structures can be described in terms of face-centered cubic packing of mercury/cadmium atoms. In our earlier work (2), we detected a new cubic phase in the Hg–As–Cl system. Based on the unit cell dimensions ($a = 12.17$ Å), we proposed the $\text{Hg}_4\text{As}_2\text{Cl}_3$ stoichiometry for this phase. However, in further investigations we found that the correct composition of this phase was $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$.

This article reports the synthesis and crystal structure

of a new mercury arsenidochloride, $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$, which has an intermediate composition between 4:2:3 (=8:4:6) and 7:4:6, and belongs to the 7:4:6 structure type. We also report the crystal structure of a known phase, $\text{Hg}_4\text{As}_2\text{Br}_3$ (3, 4), which belongs to the 4:2:3 structure type. Comparing the 4:2:3 and 7:4:6 structure types, we suggest an idealized path for the structure transformation.

EXPERIMENTAL

Synthesis. $\text{Hg}_4\text{As}_2\text{Br}_3$ was prepared by heating a stoichiometric mixture of liquid mercury, mercury dibromide, and gray arsenic in a sealed silica tube at 350°C for 7 days. Guinier photographs (Nonius FR-552 chamber, monochromatized $\text{CuK}\alpha_1$ radiation) detected a pure phase.

For the preparation of $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$, dimercury dichloride, gray arsenic, and liquid mercury were chosen as starting materials. Initially, two samples that correspond to the 4:2:3 and 7:4:6 compositions were annealed in sealed silica tubes at 300°C for 7 days. Visual analysis and Guinier photographs showed that the first sample was a mixture of traces of unreacted mercury and a new cubic phase with a unit cell parameter $a = 12.1837(8)$ Å, and the second sample was a mixture of Hg_2AsCl_2 (5), Hg_2Cl_2 , and the same cubic phase. Structure determination performed using a single crystal selected from the first sample revealed the composition $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$ for the new cubic phase. To confirm this composition, an annealing of two samples with 7.5:4:6 and 7.4:4:6 stoichiometries was undertaken under the same conditions. Guinier photographs showed that both samples were pure $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$. However, visual analysis of these samples under a $\times 28$ microscope revealed tiny drops of liquid mercury in each sample, the drops being scarcely seen in the case of the 7.4:4:6 composition. Summarizing synthetic and structural (below) data, we assigned the composition $\text{Hg}_{7.40\pm 0.01}\text{As}_4\text{Cl}_6$ to the new phase. An annealing of this compound at 330°C led to decomposition which yielded Hg_2AsCl_2 as the only ternary product.

Structure determination. Crystal structures of $\text{Hg}_4\text{As}_2\text{Br}_3$ and $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$ were each refined based on X-ray single crystal data. For this, suitable single crystals were mounted on an Enraf–Nonius CAD 4F diffractometer.

¹ To whom correspondence should be addressed. Present address: Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255.

TABLE 1
Data Collection and Refinement Parameters for
 $\text{Hg}_4\text{As}_2\text{Br}_3$, and $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$

Phase	$\text{Hg}_4\text{As}_2\text{Br}_3$	$\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$
Cell dimensions, a (Å) for space group $Pa\bar{3}$ (No. 205) at $T = 293$ K	12.610(1)	12.178(1)
$d_{\text{calc.}}$, g/cm^3	7.896	7.417
Z	8	4
Diffractometer	CAD 4F	CAD 4F
Wavelength of radiation, Å	0.71069	0.71069
μ , $1/\text{mm}$	79.486	71.635
Transmission	min 57.9% max 99.6%	min 23.4% max 99.4%
θ max. for data collection	19.98	27.95
Mode of refinement	Full-matrix least- squares on F^2	Full-matrix least- squares on F^2
No. of free parameters	28	31
Final R indices for reflections with $I > 2\sigma(I)$	$R_1 = 0.0602$ $wR_2 = 0.1039^a$ for 298 indep. reflections	$R_1 = 0.0584$ $wR_2 = 0.1323^a$ for 557 indep. reflections
Goodness-of-fit on F^2	1.049	1.102
Largest difference peak and hole, $e/\text{Å}^3$	1.612 and -1.603	3.872 and -3.435

^a Based on F^2 .

Cell dimensions were refined based on 25 well-centered reflections in the angular range $13^\circ < \theta < 17^\circ$. Collected data were corrected for Lorentz and polarization effects. Azimuthal scans of four reflections were performed to apply semiempiric absorption corrections. Systematic absences were consistent with the space group $Pa\bar{3}$ (No. 205).

For refinement of the structure of $\text{Hg}_4\text{As}_2\text{Br}_3$, initial atomic positions from the structure of $\text{Hg}_4\text{As}_2\text{I}_3$ (6) were taken and refined. Final atomic parameters were refined anisotropically by use of the program SHELXL-93 (7) to $R_1 = 0.0602$ and $wR_2 = 0.1039$.

For structure determination of $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$, direct methods (SHELXS-86 (8)) were used that gave atomic positions of two mercury atoms, two arsenic atoms, and one chlorine atom. All these atoms were refined isotropically by use of the programs SHELXL-93 (7). A difference Fourier synthesis showed one additional peak at $0, 0, \frac{1}{2}$ with a $27.5 e/\text{Å}^3$ height. Taking into account that in the structure of $\text{Hg}_7\text{Sb}_4\text{Br}_6$ (9) the same position is partially occupied by a mercury atom, we introduced this peak as a 50% occupied mercury position and refined the structure isotropically. The occupation factors of all mercury atoms were then refined independently, which revealed that occupancies of the Hg1 and Hg2 atomic positions were 100% each, and further they were kept fixed. Final anisotropic refinement of atomic parameters with the variable occupancy of the Hg3 atomic position led to $R_1 = 0.0584$ and $wR_2 = 0.1323$.

Necessary data collection and refinement parameters are summarized in Table 1. Atomic parameters are listed in Table 2, and important bonding distances and valence angles are listed in Table 3 for both structures.

RESULTS AND DISCUSSION

The crystal structure of $\text{Hg}_4\text{As}_2\text{Br}_3$ is isotypic to all pnictidehalides of cadmium (10–14) and mercury (6, 13) with the 4:2:3 composition, except for $\text{Cd}_4\text{P}_2\text{I}_3$, which exhibits orthorhombic distortion (15).

In the crystal structure of $\text{Hg}_4\text{As}_2\text{Br}_3$, there are two types of arsenic atoms. They both have tetrahedral coordination, 1As + 3Hg in the case of the As1 atoms and 4Hg in the case of the As2 atoms. The As1 atoms are joined into As–As pairs at a distance of 2.37 Å, which is usual for the cadmium/mercury arsenidehalides, which contain As_2^{4-} (5, 6, 10, 12). Each pair is surrounded by six mercury atoms forming an As_2Hg_6 octahedron. The octahedron shares each corner with one As2-centered tetrahedron, while each tetrahedron shares three of four corners with three octahedra, one corner being unshared. The view of the crystal structure of $\text{Hg}_4\text{As}_2\text{Br}_3$ as a sequence of polyhedra is shown in Fig. 1. The bromine atom bridges the Hg1 and Hg2 atoms, the Br–Hg distances being 2.806 and 2.911 Å.

The crystal structure of $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$ is similar to the structures of $\text{Cd}_7\text{P}_4\text{Cl}_6$ (16) and $\text{Hg}_7\text{Sb}_4\text{Br}_6$ (9), the latter being erroneously referred to as HgSbBr in (1). Two independent arsenic atoms each possess tetrahedral coordination of one arsenic atom and three mercury atoms. The As1 and As2 atoms are joined into pairs at a separation of 2.40 Å. Each pair is surrounded by six mercury atoms forming an As_2Hg_6 octahedron. The octahedra share all corners, forming a perovskite-like three-

TABLE 2
Atomic Parameters for $\text{Hg}_4\text{As}_2\text{Br}_3$ and $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$

Atom	Position	x/a	y/b	z/c	$U_{\text{iso/eq}}$
$\text{Hg}_4\text{As}_2\text{Br}_3$					
Hg1	24d	0.0318(1)	0.0014(1)	0.2562(2)	0.032(1)
Hg2	8c	0.2164(1)	0.2164	0.2164	0.046(2)
As1	8c	0.4458(4)	0.4458	0.4458	0.015(2)
As2	8c	0.1005(4)	0.1005	0.1005	0.014(2)
Br1	24d	0.1885(4)	0.4334(4)	0.2564(4)	0.021(2)
$\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$					
Hg1	24d	0.2177(1)	0.0260(1)	0.2891(1)	0.010(1)
Hg2	4a	0	0	0	0.015(1)
Hg3 ^a	4b	0	0	1/2	0.041(3)
As1	8c	0.2182(2)	0.2182	0.2182	0.001(1)
As2	8c	0.3319(2)	0.3319	0.3319	0.001(1)
Cl1	24d	0.4587(5)	0.0333(5)	0.2844(6)	0.015(1)

^a The occupancy of the Hg3 atomic position is $40 \pm 1\%$.

TABLE 3
Selected Bond Lengths (Å) and Angles (°) for
 $\text{Hg}_4\text{As}_2\text{Br}_3$ and $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$

$\text{Hg}_4\text{As}_2\text{Br}_3$			
As1–As1	2.37(2)	As1–As1–Hg1	108.9(2) (×3)
As1–Hg1	2.507(4) (×3)	Hg1–As1–Hg1	110.0(2) (×3)
As2–Hg2	2.53(1)	Hg1–As2–Hg1	119.87(3) (×3)
As2–Hg1	2.484(3) (×3)	Hg1–As2–Hg2	92.0(2) (×3)
Br1–Hg1	2.911(6)		
Br1–Hg1	3.240(6)		
Br1–Hg2	2.806(6)		
$\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$			
As1–As2	2.398(6)	As2–As1–Hg1	110.08(8) (×3)
As1–Hg1	2.494(2) (×3)	Hg1–As1–Hg1	108.86(9) (×3)
As2–Hg1	2.495(2) (×3)	As1–As2–Hg1	106.68(9) (×3)
Hg2–Cl1	2.705(8) (×6)	Hg1–As2–Hg1	112.11(8) (×3)

dimensional octahedral network, in which two sorts of A positions (17) of different size have different occupation. The larger sites ($4a$ position (18)) are filled with octahedral $(\text{HgCl}_6)^{4-}$ anions, while the smaller sites ($4b$ position (18)) are filled with the Hg3 atoms, which have an occupancy of 40% (Fig. 2). The total number of mercury atoms in $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$ raises a question about their oxidation states. Since the oxidation states -2 for arsenic, -1 for bromine, and $+2$ for mercury in the $24d$ position (cf. Table 2) are not in doubt, the oxidation states of mercury in the $4a$ and $4b$ positions should be

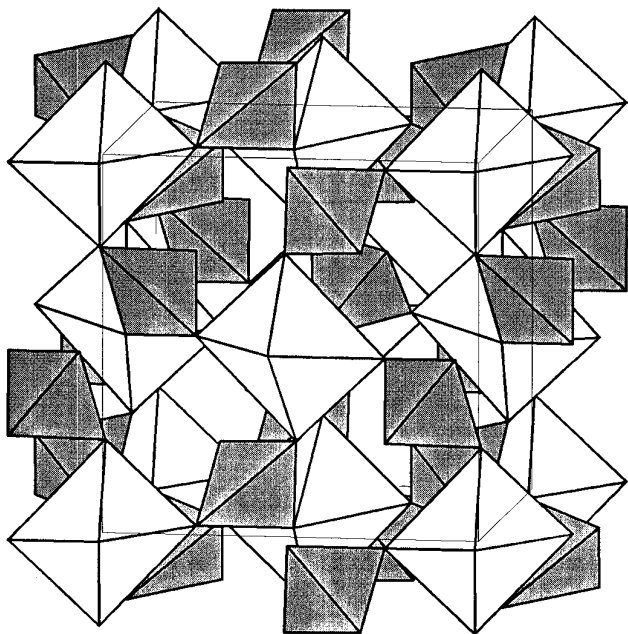


FIG. 1. Crystal structure of $\text{Hg}_4\text{As}_2\text{Br}_3$ as a sequence of As_2Hg_6 octahedra and AsHg_4 tetrahedra.

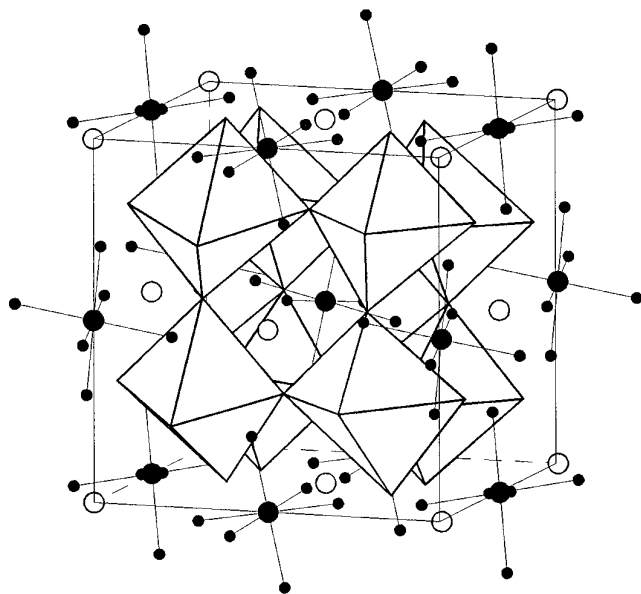


FIG. 2. Crystal structure of $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$. Origin at $1/2, 1/2, 1/2$. A perovskite-like sequence of the As_2Hg_6 octahedra is shown. Chlorine, small black circles; Hg2 atoms ($4a$ position), large black circles; Hg3 atoms ($4b$ position, 40% occupancy), open circles.

considered. In the $4a$ position, the mercury atom is surrounded octahedrally by six chlorine atoms. Such a coordination, together with the Hg–Cl distance of 2.71 \AA , is known in literature as a derivative of Hg^{2+} (17). On the other hand, the mercury atom in the $4b$ position has no neighbors up to 3.53 \AA , and possesses coordination number 14 ($6\text{Cl} + 2\text{As} + 6\text{Hg}$), which is expected for metals and alloys rather than for “normal” valence compounds. Assuming this atom to be in a zero oxidation state, we then see no reason for a limited occupation of its position. However, the synthetic procedure (above) does not allow us to expect any deviation from the $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$ composition.

It has already been noticed (6) that the crystal structure of $\text{Hg}_4\text{As}_2\text{I}_3$, as well as of other 4:2:3 cubic phases, can be described in terms of a distorted face-centered cubic packing of mercury (cadmium) atoms. Recently (19) the same type of packing was described in the structure of $\text{Hg}_7\text{Sb}_4\text{Br}_6$. As both 4:2:3 and 7:4:6 phases crystallize in the space group $Pa\bar{3}$ with close dimensions of their unit cells, there should be a clear relationship between the two structures. Figure 3 presents the idealized path of the structure transformation. In Fig. 3a, one slab of the structure of $\text{Hg}_4\text{As}_2\text{Br}_3$ is given, in which the difference between two types of arsenic atoms is shown. The As–As pairs are hidden inside the As_2Hg_6 octahedra, while the As^{3-} atoms are drawn as connected tetrahedrally with mercury atoms. When the hole structure is “squeezed,” the As^{3-} atoms come closer pairwise (Fig. 3b), finally forming additional As–As pairs, which are surrounded

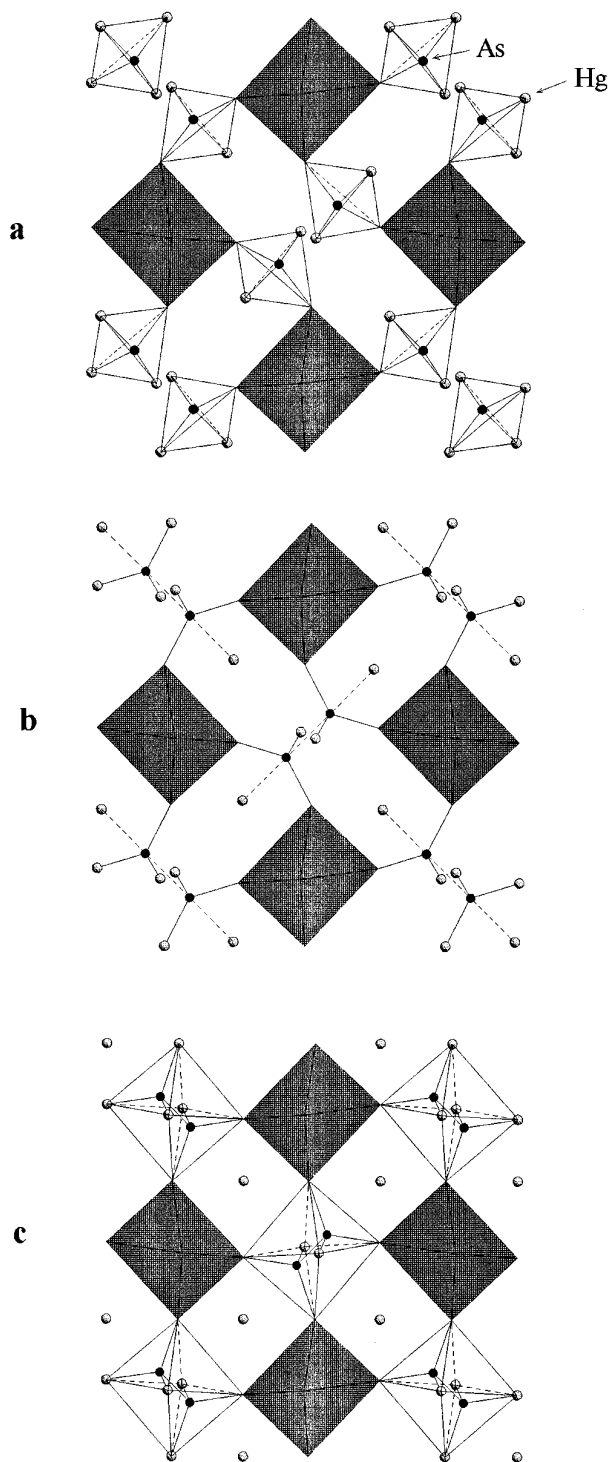


FIG. 3. An idealized path of the $4:2:3 \rightarrow 7:4:6$ structural transformation. (a) One slab of the structure of $\text{Hg}_4\text{As}_2\text{Br}_3$; (b) An intermediate (hypothetical); (c) One slab of the structure of $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$. Halogen atoms are omitted for the sake of simplicity. For explanation, see text.

octahedrally by mercury atoms (Fig. 3c). The two sorts of As_2Hg_6 octahedra now share corners as in the structure of $\text{Hg}_{7.4}\text{As}_4\text{Cl}_6$.

The structural transformation described above implies that the squeeze of the $\text{Hg}_4\text{As}_2\text{Br}_3$ structure leaves the dimensions of the As_2Hg_6 octahedra intact, is consistent with the experimental data (Table 3), but diminishes the space between the octahedra. This can occur due to the substitution of chlorine for bromine due, e.g., to the lowering of the halogen radii.

ACKNOWLEDGMENT

This work is supported by the Saint Petersburg Center for Basic Research, Russia, and by the State Program "Universities of Russia," Grant UNI-015-95.

REFERENCES

1. H. Rebbah and A. Rebbah, *J. Solid State Chem.* **113**, 1 (1994).
2. A. V. Shevelkov, E. V. Dikarev, and B. A. Popovkin, *J. Solid State Chem.* **113**, 116 (1994).
3. H. Puff and H. Gotta, *Z. Anorg. Allg. Chem.* **341**, 324 (1965).
4. Yu. Rodionov and U. R. Klokman, *Radiokhimiya* **8**, 556 (1968).
5. A. V. Shevelkov, E. V. Dikarev, and B. A. Popovkin, *Zh. Neorg. Khim.* **40**, 1496 (1995).
6. P. Labbe, M. Ledesert, and B. Raveau, *Z. Kristallogr.* **187**, 177 (1989).
7. G. M. Sheldrick, in "Crystallographic Computing 6" (H. D. Flack, L. Parkanyi, and K. Simon, Eds.), p. 111–122. Oxford Univ. Press, Oxford, 1993.
8. G. M. Sheldrick, in "Crystallographic Computing 3" (G. M. Sheldrick, C. Kruger, and R. Goddard, Eds.), pp. 175–189. Oxford Univ. Press, Oxford, 1985.
9. A. V. Shevelkov, E. V. Dikarev, and B. A. Popovkin, *J. Solid State Chem.* **98**, 133 (1992).
10. J. Gallay, G. Allais, and A. Deschanvres, *Acta Crystallogr. Sect. B* **31**, 2274 (1975).
11. H. Puff and H. Gotta, *Z. Anorg. Allg. Chem.* **343**, 259 (1966).
12. A. V. Shevelkov, E. V. Dikarev, and B. A. Popovkin, in preparation.
13. A. V. Shevelkov, E. V. Dikarev, and B. A. Popovkin, *J. Solid State Chem.* **93**, 331 (1991).
14. I. Kassama, M. Kheit, and A. Rebbah, *J. Solid State Chem.* **113**, 248 (1994).
15. A. Rebbah, J. Yazbeck, and A. Deschanvres, *Acta Crystallogr. Sect. B* **36**, 1747 (1980).
16. A. Rebbah, J. Yazbeck, and A. Deschanvres, *Rev. Chim. Miner.* **17**, 96 (1980).
17. A. F. Wells, "Structural Inorganic Chemistry," 5th ed., Clarendon Press, Oxford (1986).
18. "International Tables for X-ray Crystallography," Vol. 1, p. 314. Kynoch Press, Birmingham, 1968.
19. A. V. Shevelkov, E. V. Dikarev, and B. A. Popovkin, "Report on 14th European Crystallographic Meeting, Enschede, the Netherlands, 1992," p. 276.