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$K_4Bi_2O_5$, a Novel Ternary Oxobismuthate(III)

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$K_4Bi_2O_5$ has been synthesized as a new phase in the system K_2O/Bi_2O_3. The new potassium bismuth oxide crystallizes in space group $P\bar{1}$ with the lattice parameters $a = 569.3(2)$, $b = 952.8(4)$, $c = 978.6(2)$ pm, $\alpha = 106.47(2)$, $\beta = 105.06(2)$, and $\gamma = 106.42(3)^\circ$, $Z = 2$. The crystal structure determination (2626 diffractometer data, $R_1 = 0.039$) reveals isolated molecule anions $Bi_4O_{10}^{8-}$ (site symmetry $\bar{1}$), which consist of subunits in the sequence $[BiO_3^{3-}–BiO_2^-–BiO_2^-–BiO_3^{3-}]$. So the new compound can be regarded as a mixed ortho/metabismuthate. The cations form almost regular cubic face centered subcells. © 1998 Academic Press

INTRODUCTION

Alkali metal oxobismuthates(III) $ABiO_2$ (A = Li–Cs) and A_3BiO_3 (A = Na) have already been examined by Hoppe *et al.* (1–4). We have reinvestigated the compounds $ABiO_2$ (A = K, Rb, Cs), revised the former crystal structure determinations, and found that all compounds from sodium to caesium are isostructural (5, 6). In the A_3BiO_3 series we found K_3BiO_3 (7), which has the same crystal structure as Na_3BiO_3. Rb_3BiO_3 (7) and Cs_3BiO_3 (5) crystallize in the Na_3AsS_3 type (8, 9), and can be regarded as intermetallic phases of the Li_3Bi type filled with oxygen. In $ABiO_2$ (A = Na–Cs) the trivalent bismuth is surrounded by four (2 + 2) oxygen atoms which results from connecting BiO_2^- units to ${}^1_\infty[BiO_{2/2}O'_{2/2}]$ chains. The lone pair occupies an axial position of the pseudo-trigonal bipyramid. Apart from the alkali metal oxobismuthates only in the silver bismuthate $Ag_4Bi_2O_5$ (10) similar chains ${}^1_\infty[BiO_{1/1}O'_{3/2}]$ have been observed. In A_3BiO_3 (A = Na–Cs) bismuth has three oxygen atoms as neighbors, forming a trigonal pyramid. Regarding the lone pair as a ligand, a pseudotetrahedron is formed.

By varying the ratio of the binary oxides we have examined the system K_2O/Bi_2O_3 with respect to the existence of further potassium oxobismuthates. Our intention was to get closer insights into the characteristics of the oxygen environment of trivalent bismuth.

EXPERIMENTAL

Synthesis

$K_4Bi_2O_5$ was synthesized by solid state reaction of the binary oxides. K_2O was prepared by oxidation of distilled alkali metal with dry oxygen (11). The content of potassium was determined by flame spectroscopy (Unicam 919, Kassel, Germany) (83.1(4)%; calculated 83.0%). K_2O and Bi_2O_3 (99.9%, Acros Chimica) were mixed under argon atmosphere in a molar ratio 2:1 and placed in a silver crucible, which was closed gas tight by a conical silver plug. Heating the educt mixture for 50 h at 600°C gave colorless single crystals of $K_4Bi_2O_5$, which are sensitive to air and moisture. However, traces of $KBiO_2$ could be identified by X-ray powder diffraction. An increased molar ratio (>2:1) leads to K_3BiO_3 as a side product instead of $KBiO_2$.

Thermal Analysis

Melting points and decomposition effects were investigated by differential thermal analysis (STA 429, Netzsch, Selb, Germany). The melting temperature of the single crystals is 603°C; no decomposition is observed up to 950°C.

Structure Determination

Unit cell dimensions were determined by X-ray powder diffraction using $CuK\alpha_1$ radiation (Stadi P, Stoe & Cie, Darmstadt, Germany; germanium monochromator on the primary beam, linear PSD, external Si standard, 2θ range 5–80°).

A plate-shaped single crystal was mounted in a glass capillary under argon. The intensity data collection was carried out at room temperature on a four circle diffractometer (CAD4, Enraf–Nonius, Delft, Netherlands; $MoK\alpha$ radiation, graphite monochromator, $\lambda = 71.073$ pm). The crystal data and experimental details are listed in Table 1.

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TABLE 1
Crystal Data and Structure Refinement for $K_4Bi_2O_5$

Formula	$K_4Bi_2O_5$
Formula weight	654.35 g mol^{-1}
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	$a = 569.3(2)$ pm $\alpha = 106.47(2)°$
(from powder data)	$b = 952.8(4)$ pm $\beta = 105.06(2)°$
	$c = 978.6(2)$ pm $\gamma = 106.42(3)°$
Cell volume	$453.6(2) \times 10^6$ pm^3
Z	2
Crystal size (mm)	$0.4 \times 0.2 \times 0.06$
Calculated density	4.790 g/cm^3
μ Mo$K\alpha$	40.347 mm^{-1}
Scan	ω/θ
Theta range for data collection	0–30°
hkl (min/max)	$-8 \leq h \leq 8$ $-13 \leq k \leq 13$
	$-13 \leq l \leq 13$
Number of reflections measured	5742
Number of unique reflections	2626
Number of parameters	101
Corrections	Lorentz polarization, absorption
R_{int}[a]	0.044
$R1$[b] (all data)	0.039
w$R2$[c] (all data)	0.080

[a] $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$.

[b] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[c] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

Data reduction was carried out with the program CAD-SHEL (12), and an absorption correction (Ψ scans, MolEN, Enraf–Nonius) was applied. The structure solution (Patterson method, SHELXS-86, (13)) and refinement (SHELXL-93, (13)) led to the structure discussed below. The structure plots were prepared using DIAMOND (14).[2]

DISCUSSION OF THE CRYSTAL STRUCTURE

The positional and isotropic thermal parameters are documented in Table 2, the anisotropic displacement parameters in Table 3, and the most important interatomic distances in Table 4. Figure 1 shows the $Bi_4O_{10}^{8-}$ anion, while Fig. 2 gives an impression of the anion stacking in the triclinic and in a nonstandard unit cell (see below).

Bi(1) is surrounded by two oxygen atoms at the distance of 203 and 207 pm (BiO_2^- unit) and two further oxygen atoms at the distance of 240 and 246 pm. Regarding the lone pair as a ligand, Bi(1) is the center of a trigonal bipyramid. In accordance with the rules of Gillespie and Robinson (15) the lone pair occupies an equatorial position, and the angle between the axial oxygen atoms (168°) is smaller than 180°.

TABLE 2
Positional and Isotropic Displacement (U_{eq})[a] Parameters for $K_4Bi_2O_5$

Atom	x	y	z	$0.1U_{\text{eq}}$
Bi(1)	−0.1019(1)	0.1190(1)	0.1247(1)	12(1)
Bi(2)	0.1416(1)	0.5436(1)	0.2288(1)	12(1)
K(1)	0.3951(4)	0.2986(2)	−0.0436(2)	19(1)
K(2)	0.6307(4)	0.3795(2)	0.3681(2)	17(1)
K(3)	−0.1229(4)	0.7858(2)	0.4509(2)	23(1)
K(4)	0.3970(4)	0.9913(2)	0.3137(2)	19(1)
O(1)	0.2543(11)	0.1189(6)	0.1099(6)	14(1)
O(2)	−0.1312(12)	−0.0035(6)	0.2625(6)	17(1)
O(3)	0.1167(12)	0.3732(6)	0.3329(7)	18(1)
O(4)	0.3508(12)	0.7492(6)	0.4195(7)	19(1)
O(5)	−0.2242(12)	0.5424(6)	0.1981(7)	17(1)

[a] $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ in units of pm^2.

The second bismuth atom Bi(2) forms, together with three oxygen atoms, a trigonal pyramid (distance Bi(2)–O: 202–214 pm), or a pseudo-tetrahedron, when the lone pair is included. The O–Bi–O angles differ between 97 and 100°.

Two BiO_2^- units together with two BiO_3^{3-} units form the oligomeric anion $Bi_4O_{10}^{8-}$. The BiO_3^{3-} units take the terminal positions and are linked by the BiO_2^- units. These BiO_2^- units are connected in the same manner as in $KBiO_2$. As a result of this principle of connectivity the bipyramid around Bi(1) consists of the two short bonded terminal oxygen atoms, one oxygen atom bridging to the BiO_3^{3-} unit, one bridging oxygen atom of the second BiO_2^-, and the lone pair. The shortest Bi–O distance 202.7 pm is observed at the terminal oxygen atom O(2) of the BiO_2^- unit.

Since in $K_4Bi_2O_5$ the building units of the orthobismuthate K_3BiO_3 and the metabismuthate $KBiO_2$ are

TABLE 3
Anisotropic Displacement Parameters[a] for $K_4Bi_2O_5$ ($pm^2 \times 10^{-1}$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi(1)	15(1)	12(1)	9(1)	6(1)	4(1)	6(1)
Bi(2)	17(1)	12(1)	8(1)	6(1)	5(1)	6(1)
K(1)	26(1)	14(1)	15(1)	9(1)	5(1)	6(1)
K(2)	21(1)	19(1)	14(1)	10(1)	6(1)	7(1)
K(3)	21(1)	24(1)	17(1)	1(1)	3(1)	10(1)
K(4)	27(1)	18(1)	16(1)	11(1)	8(1)	11(1)
O(1)	20(3)	18(2)	9(2)	8(2)	10(2)	7(2)
O(2)	27(3)	17(2)	13(3)	11(2)	10(2)	8(2)
O(3)	24(3)	11(2)	13(3)	0(2)	4(2)	4(2)
O(4)	21(3)	16(2)	12(3)	3(2)	−1(2)	5(2)
O(5)	20(3)	17(2)	15(3)	9(2)	4(2)	7(2)

[a] The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$.

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[2] Further details of the structure determination have been deposited as supplementary publication No. CSD-408000 for $K_4Bi_2O_5$. Copies may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany.

TABLE 4
Selected Bond Lengths (pm) and Angles (°) for $K_4Bi_2O_5$

Bi(1)–O(2)	202.7(6)	K(1)–O(5)	262.5(6)
Bi(1)–O(1)	207.1(6)	K(1)–O(5)	265.8(6)
Bi(1)–O(3)	239.7(5)	K(1)–O(1)	267.2(6)
Bi(1)–O(1) #1	246.2(5)	K(1)–O(2)	269.7(6)
Bi(2)–O(5)	202.2(6)	K(2)–O(4)	269.1(6)
Bi(2)–O(4)	204.8(5)	K(2)–O(5)	270.4(6)
Bi(2)–O(3)	213.9(6)	K(2)–O(1)	278.6(6)
		K(2)–O(3)	283.8(7)
O(1)–Bi(1)–O(2)	98.6(2)	K(2)–O(3)	285.9(6)
O(1)–Bi(1)–O(1) #1	79.2(2)	K(2)–O(3)	289.0(7)
O(1)–Bi(1)–O(3)	91.0(2)	K(3)–O(5)	266.1(6)
O(1) #1–Bi(1)–O(2)	94.4(2)	K(3)–O(2)	267.5(6)
O(2)–Bi(1)–O(3)	94.2(2)	K(3)–O(4)	284.0(7)
O(1) #1–Bi(1)–O(3)	167.8(2)	K(3)–O(4)	289.6(6)
O(3)–Bi(2)–O(4)	100.2(2)	K(3)–O(3)	292.9(7)
O(3)–Bi(2)–O(5)	97.2(2)	K(3)–O(2)	308.9(6)
O(4)–Bi(1)–O(5)	98.7(2)	K(4)–O(1)	268.5(6)
		K(4)–O(4)	271.6(6)
		K(4)–O(4)	275.9(6)
		K(4)–O(2)	284.7(6)
		K(4)–O(2)	293.4(7)

Note. Symmetry operation #1: $-x, -y, -z$.

present at the same time, this compound may be regarded as a mixed ortho/metabismuthate(III). $K_4Bi_2O_5$ is the first 4–2–5 bismuthate with oligomeric anions. In the corresponding phase $Ag_4Bi_2O_5$ infinite chains $^1_\infty[BiO_{1/1}O'_{3/2}]$are observed.

Inspecting the first coordination sphere of bismuth there are also some more longer Bi–O bonds, which form an irregular octahedron together with the shorter bonded oxygen atoms (see Table 5). We have calculated the bond valence of these Bi–O "bonds" to test whether they contribute to the valence sum of bismuth (16). In the direction of the lone pair, two (Bi(1)) or three (Bi(2)) oxygen atoms, respectively, are linked at a distance of 370 to 420 pm with small bond valences. This six-fold coordination of bismuth is also observed in $KBiO_2$ and K_3BiO_3 and fits the concept of Brown, who developed the model of an octahedral environment for compounds of the 5th period of the main group elements with one or more lone pairs (17).

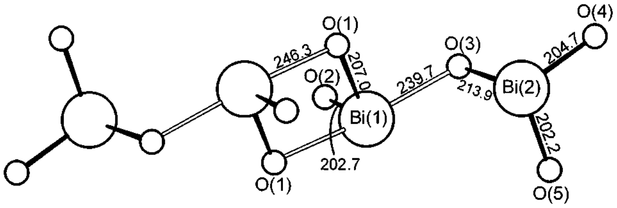

FIG. 1. The $Bi_4O_{10}^{8-}$ anion of $K_4Bi_2O_5$. Bond lengths in pm.

The coordination of the potassium ions with oxygen is not uniform; the coordination number differs between four and six. K(2) and K(3) are surrounded by six and K(4) by five oxygen atoms. The fourfold coordination of K(1) seems to be rather low; however, the ratio of anions/cations (5/6) is < 1, which necessarily leads to lower coordination numbers of the cations. Furthermore, one should keep in mind that in K_2O the potassium ions are also surrounded by only four oxygen ions.

The anion BiO_2^- and the cation IO_2^+ have the same number of valence electrons. In $(IO_2)_2S_2O_7$ this cation is linked with another IO_2^+-cation in the same way as the BiO_2^- in $K_4Bi_2O_5$ (18).

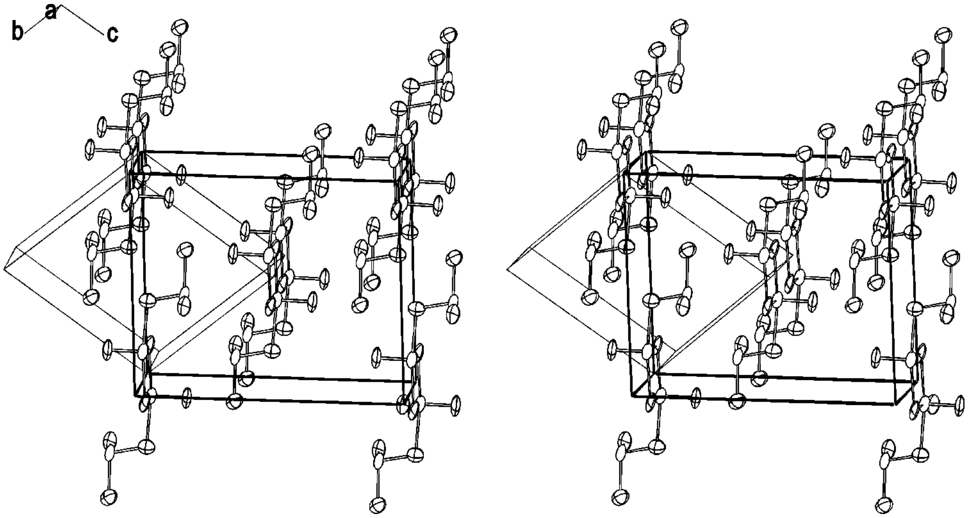

FIG. 2. Package of the $Bi_4O_{10}^{8-}$ anions relative to the conventional and to a pseudo-orthogonal, body-centered unit cell (stereo pair). Empty thermal ellipsoids, Bi; ellipsoids with octands, O. The potassium ions which separate the anions have been omitted.

TABLE 5
Bond Lengths (pm) and Bond Valences v of the Coordination Polyhedron of Bismuth for $K_4Bi_2O_5$

	d	*v*		*d*	*v*
Bi(1)–O(2)	202	1.176	Bi(2)–O(5)	203	1.084
Bi(1)–O(1)	205	1.114	Bi(2)–O(4)	207	1.056
Bi(1)–O(3)	214	0.874	Bi(2)–O(3)	240	0.433
Bi(1)–O(1)	370	0.013	Bi(2)–O(5)	246	0.368
Bi(1)–O(1)	416	0.004	Bi(2)–O(1)	363	0.016
Bi(1)–O(5)	420	0.003	Bi(2)–O(5)	418	0.003

The molecular building principle as found for the $Bi_4O_{10}^{8-}$ anion seems to be generizable; this encourages us to synthesize further compounds with even longer chains of BiO_2^- units terminated by BiO_3^{3-}.

Finally, it should be noted that the cations Bi^{3+} and K^+, if regarded as identical species, form an almost ideal cubic closest package. To visualize this phenomen, the triclinic unit cell was transformed to the unconventional space group $I\bar{1}$ by applying the matrix T:

$$T = \begin{pmatrix} 1 & 0 & 0 \\ 1 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}, \quad \det(T) = 2.$$

Now the lattice constants $a' = 569.3$, $b' = 1031.8$, $c' = 1547.3$ pm, $\alpha' = 87.90$, $\beta' = 89.44$, and $\gamma' = 87.46°$ describe an almost rectangular cell. In Figs. 2 and 3 the standard setting as well as the chosen unconventional unit cell are shown; the metal ions form almost regular face-centered cubic subcells with lattice constants of about 533 pm. The oxygen anions are located in the octahedral interstices (Fig. 4). They are shifted, however, from the centers of gravity toward the Bi^{3+} cations.

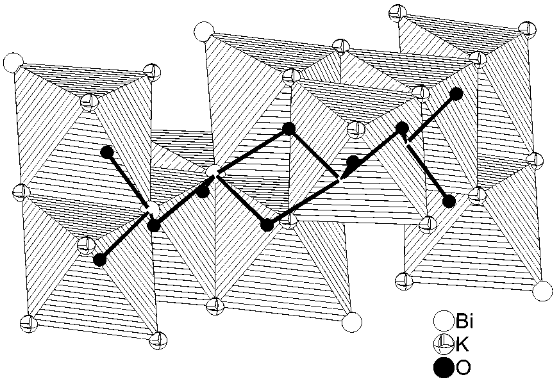

FIG. 4. Octahedral coordination of the 10 oxygen anions of one $Bi_4O_{10}^{8-}$ unit. The distorted octahedra are formed by Bi^{3+} and K^+ ions; the O^{2-} are significantly shifted toward Bi^{3+}.

This way of interpreting nonmolecular crystal structures has already been discussed in detail by O'Keeffe and Hyde (19). The authors regard the most important inorganic oxides as cation arrays with anions inserted into the interstices. Over this, it was found that the cation arrays alone form arrangements as in alloy structures. In recently published papers, Vegas *et al.* (20, 21) also state that in oxyhydroxides of trivalent metals as well as in garnet-type and perovskite-like compounds the cationic arrays can be related to the parent metallic phases.

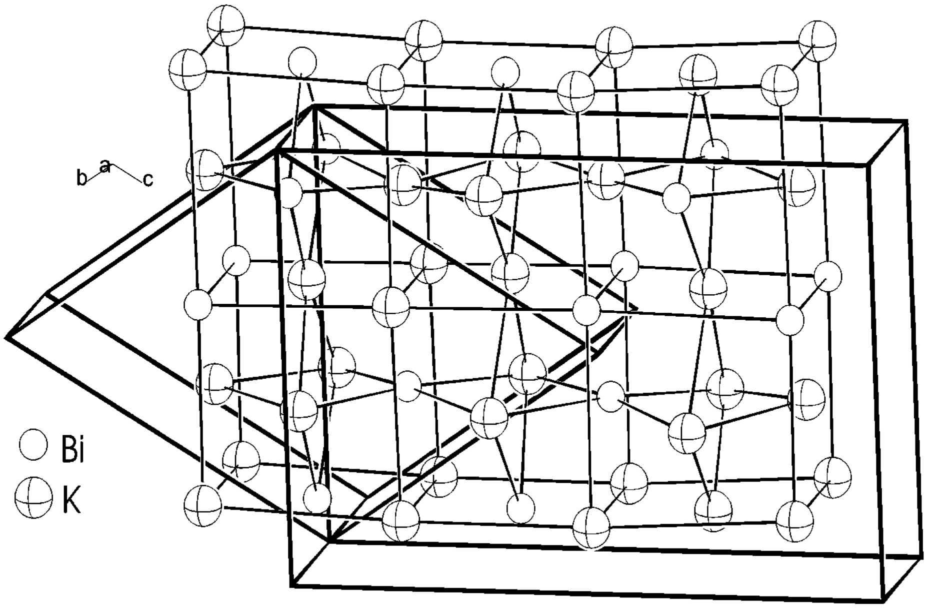

FIG. 3. Unit cell of $K_4Bi_2O_5$ in the conventional ($P\bar{1}$) and the unconventional ($I\bar{1}$), almost rectangular setting. Oxygen ions have been omitted. The cations alone form pseudo-cubic face-centered subcells with lattice constants of about 533 pm.

TABLE 6
Distances (pm) in Intermetallic Phases Compared with Metal–Metal Distances in $K_4Bi_2O_5$

	K_3Bi (19)	KBi_2 (20)	$K_4Bi_2O_5$
Bi–Bi	—	336	350 … 412
K–K	365 … 401	411	339 … 419
Bi–K	357 … 401	394	360 … 402

Unfortunately, an intermetallic phase "K_2Bi" is still unknown. However, even the intermetallic distance ranges in K_3Bi and KBi_2 (22, 23) are in good agreement with those in $K_4Bi_2O_5$ (see Table 6).

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