The First Quaternary Oxobismuthate(V): KLi$_6$BiO$_6$

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The new compound KLi$_6$BiO$_6$ has been prepared by heating pulverized mixtures of K$_2$O, Li$_2$O$_2$ and Bi$_2$O$_3$ (Ni cylinder, 20 d, 680 °C). The nearly colourless single crystals are trigonal–rhombohedral, space group $R\bar{3}m$, $a = 841.6$, $c = 729.3$ pm and $Z = 3$. Four-circle diffractometer data yielded final discrepancy factors $R = 1.9\%$ and $R_w = 1.8\%$. KLi$_6$BiO$_6$ is a stuffed derivative of the α-Li$_6$UO$_6$ structure type. The Madelung Part of the Lattice Energy (MAPLE) and Effective Coordination Numbers (ECoN), the latter derived from Mean Fictive Ionic Radii, MEFIR, have been calculated and are discussed.

Dedicated to Prof. Sten Andersson on the occasion of his 60th birthday.

Little is yet known concerning the synthesis, properties and structure of alkali metaloxobismuthates. This has experimental origins: structure determinations on single crystals of oxobismuthates(III) have only been obtained for ABiO$_2$ (A = Li–K),[1-3] Li$_3$BiO$_3$[4] and Na$_3$BiO$_3$,[5] and the structures of RbBiO$_2$[3] and CsBiO$_2$[3] remain unsolved. Our present knowledge of oxobismuthates(V) is even less. Red KBiO$_3$[6] contains water and is in fact KBiO$_3$·$^1/_3$H$_2$O. Unhydrated red KBiO$_3$ was recently prepared as a powder by Jansen.[7] Only the Bi sites have been reported for yellow Li$_3$BiO$_4$.[8] Structural data for the deep-yellow Na$_3$BiO$_4$[9] need to be verified, because only integrated Weissenberg intensities were used. Despite numerous attempts at their synthesis, polynary oxides such as K$_2$LiBiO$_3$ or KLi$_2$BiO$_3$ are still unknown. However, during a series of experiments attempting to prepare K$_2$LiBiO$_3$ we surprisingly obtained KLi$_6$BiO$_6$.

Experimental

The reaction of mixtures of Li$_2$O$_2$ [prepared by using LiOH (Merck, >99%) and H$_2$O$_2$ (Merck)],[10] K$_2$O [prepared by oxidizing K metal (Merck, >98%) which was purified by segregation][11] and Bi$_2$O$_3$ [prepared by heating BiONO$_3$ (Fluka, p.a.) at 350 °C] in the ratio K:Li:Bi = 2:2:1 leads to a colourless product (Ni cylinder, 680 °C, 20 d). In addition to many single crystals of K$_2$O and Li$_2$O, we obtained only a small number of single crystals of the pale yellow KLi$_6$BiO$_6$.

The preparation of powders of KLi$_6$BiO$_6$ was very difficult. We obtained good samples by heating mixtures of 'K$_2$O$_3$', Li$_2$O and Bi$_2$O$_3$ (K:Li:Bi = 0.8:4:0.5) (Au cylinder, 500 °C, 10 d).

Crystal structure determination

A suitable crystal for X-ray diffraction was chosen under paraffin (dried with Na). The quality of the crystal was confirmed by film methods (precession photographs of $hk0$, $hk1$, $h0l$ and $h1l$). The crystal belongs to the rhombohedral system. The lattice constants were derived from powdered samples on a Guinier–Simon photograph (Table 1): $a = 841.6$, $c = 729.4$ pm and $c/a = 0.867$.

The experimental data are compiled in Table 2. Tables 3 and 4 contain the positional and thermal parameters. Structure factors are available from the authors upon request.

Discussion and description of the structure

The compounds α-Li$_6$UO$_6$[11] and Li$_6$TeO$_6$[12] prepared recently are not completely isotypic. In addition to the octahedral part [MO$_6$] with M = U,Te, there is a small differ-

Table 1. KLi$_6$BiO$_6$: evaluation of the Guinier–Simon photograph (Cu K_α radiation, $\lambda = 154.178$ pm, no separation of the $K_{\alpha 1}/K_{\alpha 2}$ doublets, calibrated with quartz, $a = 491.25$, $c = 540.43$ pm, $T = 25$ °C.[a]

$h k l$	$4\Theta_o/°$	$4\Theta_c/°$	$\sin^2\Theta_o \times 10^3$	$\sin^2\Theta_c \times 10^3$	I_o	I_c
1 0 1	34.66	34.30	22.70	22.23	100	100.0
1 1 0	42.31	42.13	33.70	33.42	80	97.1
0 1 2	54.82	54.51		55.52	80	62.6
2 1 0		54.58		55.65		43.9
2 0 2	69.58	69.40	89.38	88.94	20	23.4
2 1 1		69.46		89.08		11.6
0 0 3		73.68		99.85		1.4
3 0 0	73.99	73.84	100.67	100.26	20	26.3

[a]For additional data see Ref. 22.

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Table 2. KLi$_6$BiO$_6$, crystallographic and analytical data.

Formula	KLi$_6$BiO$_6$
Molecular weight/g mol^{-1}	385.72
Crystal system	rhombohedral
Space group	$R\bar{3}m$, No. 166
Lattice constants/pm (Guinier–Simon data)	$a = 841.6(2)$ $c = 729.4(2)$ $c/a = 0.866$
Z	3
Molecular volume/cm^3 mol^{-1} (determined by X-ray diffraction)	89.8
Density/g cm^{-3} (determined by X-ray diffraction)	4.294
Crystal form, colour	irregular, pale yellow
Data collection	Philips PW 1100 four-circle diffractometer, graphite monochromator; AgK_α radiation ($\lambda = 56.09$ pm), ω-scan, scan speed 0.065° s^{-1}, scan width 1.95°, Θ-range $3° \le \Theta \le 26°$, $F(000) = 483$, $\mu = 1.45$ cm^{-1}
Data correction	background, polarization, Lorentz factor, absorption
Statistics	242 independent $I_0(hkl)$ out of 3821 $I_0(hkl)$, 17 free parameters
Structure determination	program SHELXS-86: Patterson (Bi^{5+}, K$^+$); program SHELX-76: difference Fourier (Li$^+$ and O^{2-}); full matrix least-squares refinement $R = 1.9\%$, $R_w = 1.8\%$ ($k = 1.0$, $g = 0.001$), $w = k(\sigma_2(F) + gF^2)^{-1}$

Fig. 1. Ortep drawing of the vacancy in Li$_6$TeO$_6$.

Table 3. Wyckoff positions and positional parameters of KLi$_6$BiO$_6$ (e.s.d.s in parentheses).

Atom	Wyckoff position	x	y	z
K	3b	0.0000	0.0000	0.5000
Bi	3a	0.0000	0.0000	0.0000
Li	18f	0.6549(12)	0.0000	0.0000
O	18h	0.1226(3)	0.8774(3)	0.1555(5)

Fig. 2. Ortep drawing of the vacancy in α-Li$_6$UO6.

Table 4. Mean displacement parameters U_{ij} (in pm^2) of KLi$_6$BiO$_6$ (e.s.d.s in parentheses).[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{21}	U_{13}
K	198(8)	198(8)	215(14)	0	0	99(4)
Bi	60(2)	60(2)	32(2)	0	0	30(1)
Li	131(28)	117(37)	107(36)	23(29)	11(15)	58(18)
O	113(10)	113(10)	98(13)	6(5)	-6(5)	53(12)

[a]The U_{ij} are defined for exp $[-2\pi^2(U_{11}h^2a^{*2} + ... + U_{12}hka^*b^*)]$.

ence in the coordination of Li (Tables 5 and 6). However, in both cases there is a large vacancy which could be filled by K$^+$, for example. All attempts by reactions such as K + Li$_6$UO$_6$ → KLi$_6$UO$_6$ to obtain derivatives of U^{5+} were without success. It is important to note that the form of vacancy in Li$_6$TeO$_6$ is remarkably different from that of Li$_6$UO$_6$ (Figs. 1 and 2). We then turned to Ir^{5+}, for which KIrO$_3$,[13] whose structure has been characterized, proves the existence of Ir^{5+} in oxides, and immediately obtained (starting with K$_4$IrO$_4$[14] under appropriate conditions) KLi$_6$-IrO$_6$,[15] where the geometry of CP(K) corresponds exactly to that of the vacancy in α-Li$_6$UO$_6$. KLi$_6$BiO$_6$ is isotypic with KLi$_6$IrO$_6$, indicating the expected relationship be-

Table 5. Motifs of mutual adjunction of α-Li₆UO₆.ᵃ

	18 O	CN	ECoN ΣM/ΣO	MEFIR /pm
3 U	6/1 208	6	6.0	68.5
18 Li	1/1+1/1+1/1+1/1 194 195 200 202	4	3.9	57.7
CN	5			
ECoN	4.9			
MEFIR/pm	140.1			

ᵃECoN and MEFIR starting values of ionic radii: standard value $R(O^{2-})$ = 140 pm; the values for the cations were calculated from weighted distances d(cation–O^{2-}) − 140 pm: $R(U^{6+})$ = 68.5 pm, $R(Li+)$ = 57.6 pm. Agreement between starting and final values is excellent.

Table 6. Motifs of mutual adjunction of Li₆TeO₆.ᵃ

	18 O	CN	ECoN ΣM/ΣO	MEFIR /pm
3 Te	6/1 193	6	6.0	52.6
18 Li	2/2+2/2+1/1 195 206 238	5	4.3	62.1
CN	6			
ECoNᵇ	5.3			
MEFIRᵇ/pm	140.1			

ᵃECoN and MEFIR starting values of ionic radii: standard value $R(O^{2-})$ = 140 pm; the values for the cations were calculated from weighted distances d(cation–O^{2-}) − 140 pm: $R(Te^{6+})$ = 52.6 pm, $R(Li+)$ = 62.1 pm. Agreement between starting and final values is excellent.

Table 7. Motifs of mutual adjunction of KLi₆TaO₆.ᵃ

	18 O	CN	ECoN ΣM/ΣO	MEFIR /pm
3 Ta	6/1 212	6	6.0	72.0
3 K	6/1 + 6/1 308 + 309	12	12.0	168.3
18 Li	2/2+2/2 195 + 198	4	4.0	56.7
CN	7			
ECoNᵇ	7.0			
MEFIRᵇ/pm	140.1			

ᵃECoN and MEFIR starting values of ionic radii: standard value $R(O^{2-})$ = 140 pm; the values for the cations were calculated from weighted distances d(cation–O^{2-}) − 140 pm: $R(Ta^{5+})$ = 61.4 pm, $R(K+)$ = 168.3 pm, $R(Li+)$ = 55.1 pm. Agreement between starting and final values is excellent.

Table 8. Motifs of mutual adjunction of KLi₆IrO₆.ᵃ

	18 O	CN	ECoN ΣM/ΣO	MEFIR /pm
3 Ir	6/1 200	6	6.0	59.6
3 K	6/1 + 6/1 295 + 307	12	11.8	160.4
18 Li	2/2+2/2 193 + 195	4	4.0	53.6
CN	7			
ECoNᵇ	7.0			
MEFIRᵇ/pm	140.2			

ᵃECoN and MEFIR starting values of ionic radii: standard value $R(O^{2-})$ = 140 pm; the values for the cations were calculated from weighted distances d(cation–O^{2-}) − 140 pm: $R(Ir^{5+})$ = 59.6 pm, $R(K+)$ = 160.4 pm, $R(Li+)$ = 55.0 pm. Agreement between starting and final values is excellent.

Table 9. Motifs of mutual adjunction of KLi₆BiO₆.ᵃ

	18 O	CN	ECoN ΣM/ΣO	MEFIR /pm
3 Bi	6/1 212	6	6.0	72.0
3 K	6/1 + 6/1 308 + 309	12	12.0	168.3
18 Li	2/2 + 2/2 195 + 198	4	4.0	56.7
CN	7			
ECoNᵇ MEFIRᵇ/pm	7.0 140.1			
ECoNᶜ MEFIRᶜ/pm	8.1 152.0			
ECoNᵈ MEFIRᵈ/pm	13.8 144.3			

ᵃECoN and MEFIR starting values of ionic radii: standard value $R(O^{2-})$ = 140 pm; the values for the cations were calculated from weighted distances d(cation–O^{2-}) − 140 pm: $R(Bi^{5+})$ = 71.92 pm, $R(K+)$ = 168.25 pm, $R(Li+)$ = 56.63 pm. ᵇO/Σ(M). ᶜO/Σ(O). ᵈO/Σ(M+O). Agreement between starting and final values is excellent.

tween elements of the 5th Main Group and the 6th Transition Group of the Periodic Table.

Obviously we found with KLi₆MO₆ a new type of structure which can be adopted quite generally provided M⁵⁺ fits by size [MEFIR(M⁵⁺) = 50–70 pm, Tables 5–9]. This is shown by KLi₆TaO₆,[16] which we recently synthesized accordingly. To show the similarity of structures we give in Table 7 the motifs of mutual adjunction.
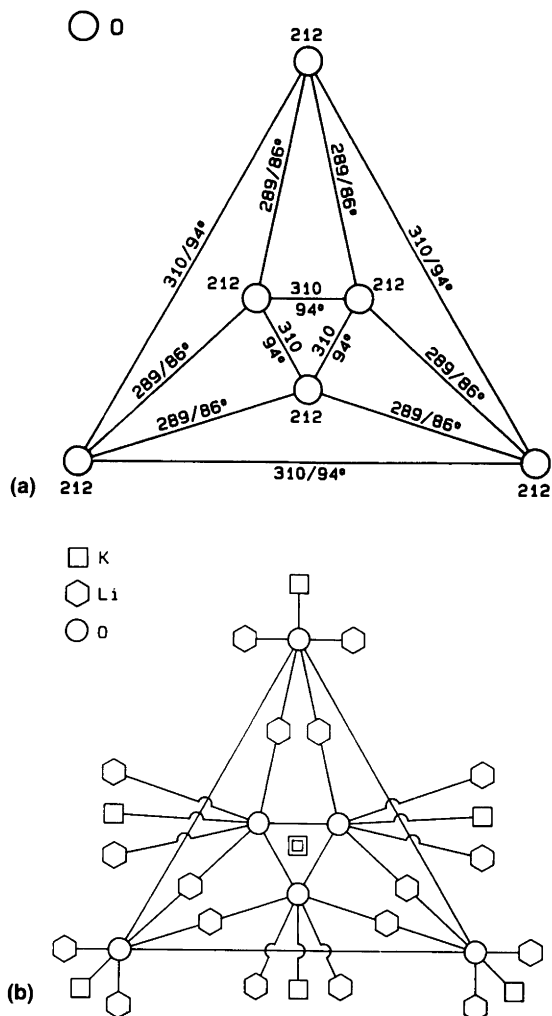
Fig. 3. (a) Schlegel projection and (b) Schlegel diagram of CP(Bi). (☐ denotes K in both the front and back of the polyhedron.)

Fig. 4. (a) Schlegel projection and (b) Schlegel diagram of CP(Li).

Primary structure. Bi^{5+} is surrounded by a slightly distorted octahedron of O^{2-}, where the distortion only affects angles (O–Bi–O), whereas the distances are equal. The bond distances and angles are given in form of a Schlegel projection.[17] The polyhedra are drawn so that there are no intersections between the lines. The central atom is not drawn in the projection. The distances d(central-atom–ligand) are given at the terminal positions; the distances d(ligand–ligand) and their corresponding angles ∢(ligand–central-atom–ligand) are reported next to the edges. The Schlegel diagrams show the nearest and next-nearest neighbours of the polyhedron. The values of CP(Bi) are given in Fig. 3(a). Li$^+$ has tetrahedral coordination [Fig. 4(a)]. The coordination polyhedron of K$^+$, CP(K), is quasi-icosahedral [Fig. 5(a)], where, unlike a true icosahedron, the six equatorial oxygen atoms form a slightly puckered plane with atom positions alternating ±8.2 pm out of the plane (Fig. 6).
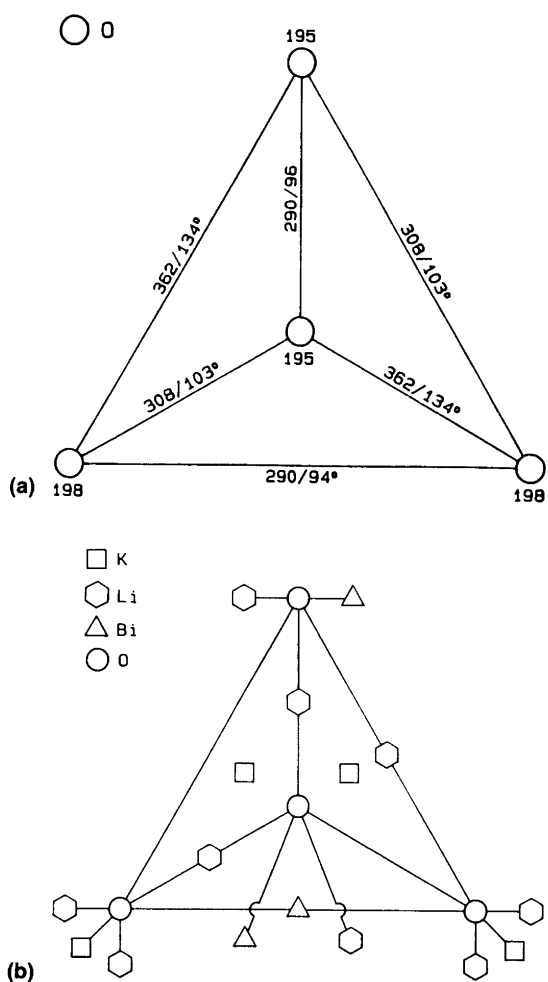
Secondary structure. The polyhedra CP(Bi) are 'isolated', the smallest distance d(Bi–Bi) being 544.2 pm [Fig. 3(b)]. The polyhedron CP(K) is connected via common ligands O^{2-} with six further polyhedra CP(K) resulting in a close packing of KO$_{12}$ polyhedra [Fig. 5(b)]. The distances d(K–K) are 544.2 pm (6×) and 688.8 pm (6×). If one counts all 12 corresponding CP(K) as equal, then the form of cubic closest packing is obtained. CP(Li) is connected to six identical polyhedra via O^{2-} apically and to three other polyhedra via common edges [Fig. 4(b)].

Tertiary structure. The polyhedra CP(Bi) and CP(K) share triangular faces and form chains running parallel to the hexagonal *c*-axis (Fig. 7). These chains are arranged with the form of close-packed tree trunks. The vacancies within this close packing are filled by Li$^+$ (Fig. 8).

Motifs of mutual adjunction, ECoN and MEFIR

The results of ECoN,[18] MEFIR[18] and the motifs of mutual adjunction are given in Table 8. The correlation between
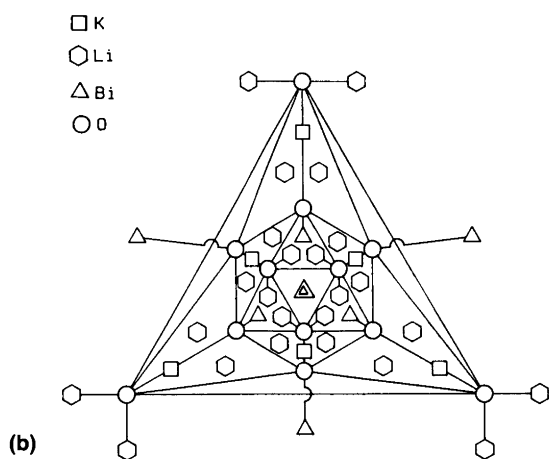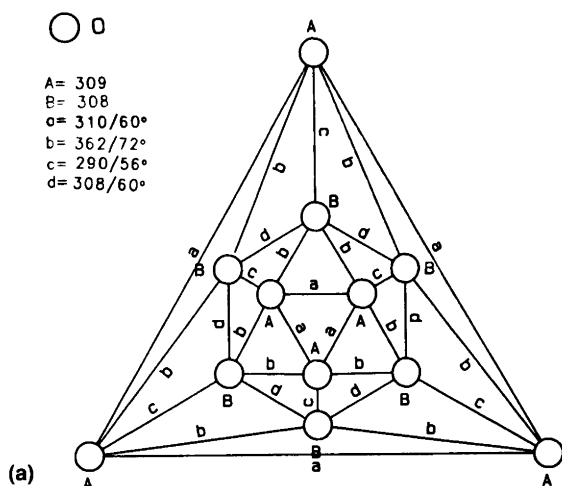
○ O

A= 309
B= 308
○= 310/60°
b= 362/72°
c= 290/56°
d= 308/60°

(a)

Fig. 6. Ortep drawing of CP(K) with thermal ellipsoids.

□ K
○ Li
△ Bi
○ O

(b)

Fig. 5. (a) Schlegel projection and (b) Schlegel diagram of CP(K). (⬙ denotes Bi in both the front and back of the polyhedron.)

Fig. 8. Connections between –Bi–K–Bi– chain and LiO₄; some of the CP(Li) are omitted for clarity.

The Madelung Part of the Lattice Energy, MAPLE[19]

ECoN and a simple counting of coordination numbers is very good, especially for oxygen, despite a pronounced diversity in bond distances. Additional interatomic distances are given in Table 10.
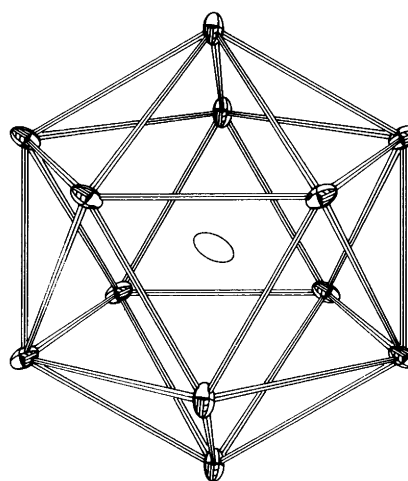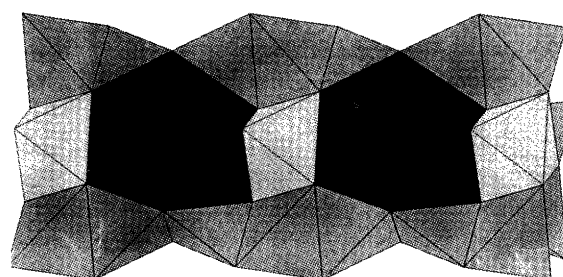
In solid-state chemistry the theoretical calculation of standard values of ΔH°_{298} with sufficient accuracy is generally still impossible. In the case of compounds such as oxides and fluorides of metals the Born–Haber cycle[20] is recommended. Nevertheless, the insufficient exactness is striking. In case of oxides quantities such as $\Delta H^{\circ}_{298}(O^{2})$ are
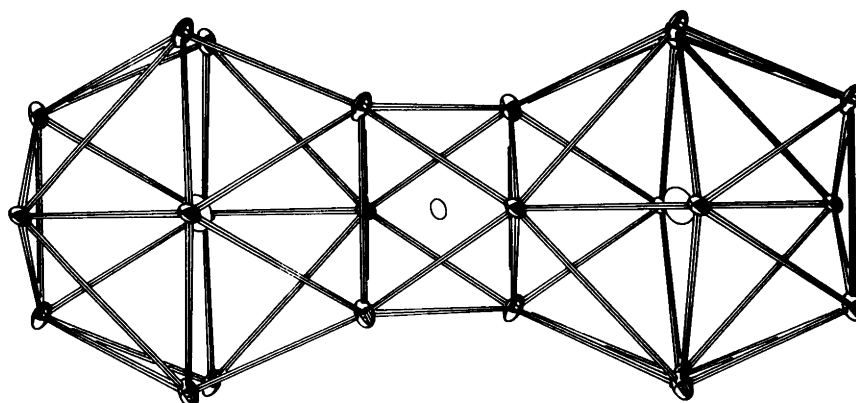

Fig. 7. Ortep drawing of –Bi–K–Bi– chains along [001].

Table 10. Bond distances of KLi_6BiO_6.[a]

	Bi	K	Li
Bi	544.2 (6×)	365.6 (2×)	290.8 (6×)
K	365.6 (2×)	544.2 (6×)	301.8 (12×)
	501.6 (6×)		467.2 (12×)
Li	290.8 (1×)	301.8 (2×)	244.4 (2×)
	368.3 (2×)	467.2 (2×)	261.1 (1×)

[a]Additional distances: d(O–O) = 289.4 (2×); 290.2 (1×);
308.0 (2×).

Table 11. MAPLE values of KLi_6BiO_6.[a]

	d_{min}	Partial Madelung factor	MAPLE	¹MAPLE[b]
Bi^{5+}	212.0	15.38	2649.5	206.8
K^+	308.0	0.62	106.6	208.0
Li^+	349.4	1.05	179.0	349.4
O^{2-}	265.4	3.19	544.0	265.4

[a]Madelung factor: 41.73. Coulomb part of the lattice energy:
7094.3 kcal mol⁻¹. [b]¹MAPLE = MAPLE × d_{min} × charge⁻².

uncertain. All estimates (in the range 220–240 kcal mol⁻¹) are based on extrapolations involving all known imponderabilities which are connected with such a calculation. Nevertheless, the Madelung Part of the Lattice Energy, MAPLE, can be used if one intends to compare similar compounds.

Obviously, ΔH°_{298} values of different modifications of a given compound, which can be obtained and handled under normal conditions, must be very similar. Thus we understand why this holds for MAPLE values of all forms of, e.g., TiO_2 (MAPLE = 3253.3 kcal mol⁻¹). With solid-state reactions we have in our field cases such as $BaO + TiO_2 \rightarrow BaTiO_3$ (all solid). Here the enthalpy of reaction ΔH°_{298} is small (see above) compared with the lattice energies (and therefore the MAPLE values of the binary constituents).

This is this why generally in such cases the MAPLE of polynary fluorides or oxides equals the sum of the MAPLE contributions of the binary constituents [BaO: 839.9 kcal mol⁻¹; TiO_2 (rutile): 3253.3 kcal mol⁻¹; $BaTiO_3$: 4110.7 kcal mol⁻¹ (Δ = 17.5 kcal mol⁻¹; 0.4%)]. If we assume $\Delta H^{\circ}_{298}(O^{2-}, g)$ = 230 kcal mol⁻¹, then from well known thermochemical data the lattice energies E_L are −759 kcal mol⁻¹ (BaO, 90% of MAPLE), −2905 kcal mol⁻¹ (TiO_2, 89% of MAPLE) and −3664 kcal mol⁻¹ ($BaTiO_3$, 89% of MAPLE). With $BaO(s) + TiO_2(s) \rightarrow BaTiO_3(s)$ we have correspondingly ΔH°_{298} (reaction) = −40 kcal mol⁻¹, i.e. 1.1% of $E_L(BaTiO_3)$. It is this relatively small heat of formation from binary constituents which shows why and when the concept of MAPLE holds.* The difference is usually $\Delta \leq 1$%. On the other hand, Cs_2SO_4 [ΔH°_{298}(reaction) = −153 kcal mol⁻¹, $E_L(Cs_2O)$ = −532 kcal mol⁻¹, $E_L(SO_3, s)$ = −7453 kcal mol⁻¹ and $E_L(Cs_2SO_4, s)$ = −8138 kcal mol⁻¹] shows (Δ = +2%) that the limits of the concept of MAPLE should and will be reached, and that discrepancies with MAPLE are understandable.

It is surprising that such relationships hold even in case of other halogenides and chalcogenides. The structure of Bi_2O_5 is still unknown. Therefore it is impossible to compare the MAPLE values for the quaternary oxide KLi_6BiO_6 with the binary oxides. However, we can compare known

Table 12. Shortest bond distances d(Cs–O) and d(Cs–B) (in pm) of $Cs_3NaLi_2[BO_3]_2$.[27]

d(Cs1–O):	294, 307, 324, 331, 345, 357, 376
d(Cs1–B):	343, 372
d(Cs2–O):	295, 298, 305, 312, 315, 322, 336
d(Cs2–B):	320
d(Cs3–O):	295, 298, 318, 338, 355, 260 (2×), 366, 370, 383, 385
d(Cs3–B):	341, 351

structural information in the following way. With Na_3BiO_4 we have eqn. (1), and correspondingly for KLi_6BiO_6 we have eqn. (2). The correlation between both values is sufficient, considering the limits of accuracy of the structural determination of Na_3BiO_4 (I_0 from integrated Weissenberg photographs only).

$$2 \times \text{MAPLE}(Na_3BiO_4) - 3 \times \text{MAPLE}(Na_2O) = \text{MAPLE}(Bi_2O_5) \approx 8453.8 \text{ kcal mol}^{-1} \quad (1)$$

$$2 \times \text{MAPLE}(KLi_6BiO_6) - \text{MAPLE}(K_2O) - 6 \times \text{MAPLE}(Li_2) = \text{MAPLE}(Bi_2O_5) \approx 8577.4 \text{ kcal mol}^{-1} \quad (2)$$

A critical remark on charge distribution

The well known idea of Pauling to interpret distances between adjacent C atoms in molecules via bond order using eqn. (3) has been extended not only to other mole-

$$d_n = d_1(1 - \ln n)^{1/6} \quad (3)$$

cules containing other elements, but to solid-state chemistry.[23] This must be generally wrong, because we have compounds such as $K_7Th_6F_{31}$, where one of the 31 F⁻ is neither connected to Th^{4+} nor to K⁺ but surrounded by 12 other F⁻ only.[24-26] Another striking example is our new borate $Cs_3NaLi_2[BO_3]_2$.[27] Here several structure-determining distances d(Cs–O) are clearly longer than shortest distances d(Cs–B) (Table 12).

The results will therefore hold for our attempt to answer such questions by concepts like CHARDI,[28] where initially we found surprising agreement between given and calcu-

*All calculations are made for ionic models such as $Ba^{2+}O^{2-}$ and $Ba^{2+}Ti^{4+}O_3^{2-}$.

lated amounts of charges (oxidation states). A more extended discussion of this subject will be given elsewhere.

Closing remarks

The results of our experiments are surprising. We believed, guided by experience and a knowledge of the literature, that oxobismuthates(V) should exhibit a coordination number of 4 only for Bi^{5+} and always to be deep red–orange in colour. As we know now, this may hold for oxides of the type Na$_3$BiO$_4$ and its derivates (e.g. the unknown CsBaBiO$_4$). One again we notice how dangerous it is to believe that incredible things can not be realized.

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