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New Routes in the Synthesis of Metal Oxides, II*

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XIII. Tailor-Made Synthesis

Despite the fact that "NiO" (*84*) adopts the NaCl type structure, in striking contrast to HgO, both $K_2[NiO_2]$ (*4*) and $K_2[HgO_2]$ (*85*) exhibit the same XeF_2-like grouping with remarkably short distances, d(Ni—O) = 168 and d(Hg—O) = 193 pm. For this reason we ask whether a similar grouping $[AgO_2]^{2-}$ exists in corresponding oxides. Although "AgO" (*86*) (which should be reinvestigated) and Ag_2O_3 (*87*) exist, no oxoargentate(II) nor (III) is known. With the present knowledge it is just a conjecture that Ag^{2+} as well as Ag^{3+} oxidizes O^{2-} to O_2^{2-} or O_2^-. We encounter a similar situation with Ni^{III}. In striking contrast to the existence of $BaNi^{IV}O_3$ (*88*), no $A[NiO_2]$ with A = K, Rb, or Cs is known. Only $K_9[Ni^{III}O_4][Ni^{II}O_3]$ (*89*) and $K_3Ni^{II}Ni^{III}O_4$ (*90*) have been reported. In the former case we encounter a tetrahedron as with $Na_4[CoO_4]$ (*91*) and a planar group as with $Na_4[FeO_3]$ (*92*), $Na_4[CoO_3]$ (*93*), as well as $K_4[ZnO_3]$ (*43*). In light of the above we decided first to synthesize $KNa_2[CuO_2]$, because with Cu_2O all experiments are much easier, and then to attempt the synthesis of $KNa_2[AgO_2]$ (*94, 95*).

XIV. The Role of Vacancies

Like many other structural types of molecular compounds, XeF_2 shows vacancies. In the $[\overset{5}{L}]_2[\overset{4}{L}]_2[XeF_2]$ arrangement two different types occur. The first set is occupied by A^+ as in $A_2[NiO_2]$ and $A_2[HgO_2]$ (A = K, Rb, or Cs). In $Li_2[HgO_2]$ probably the second type is filled. So $KNa_2[CuO_2]$ with $\overset{5}{K}[\overset{5}{L}]\overset{4}{Na_2}[CuO_2]$ might be a "stuffed derivative" of the XeF_2 type with still one vacancy $[\overset{5}{L}]$ empty. As shown by single crystal work (*94*), $KNa_2[CuO_2]$ adopts this new tetragonal structure as foreseen (see Table XXIV); from powder data we infer that $KNa_2[AgO_2]$ (*95*) is isotypic.

XV. New Oxouranates

Another illustrative example of the role of vacancies is α-Li_6UO_6. We have elucidated its crystal structure in the course of a

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TABLE XXIV

MOTIFS OF MUTUAL ADJUNCTION OF KNa_2CuO_2

	1	1	C.N.
1 K^+	1/1 (274.4)	4/4 (317.0)	5
2 Na^+	2/4 (227.8)	2/4 (245.7)	4
1 Cu^+	1/1 (182.4)	1/1 (173.1)	2
C.N.	6	9	

more detailed study of new uranates of the heavier alkali metals. In $[L^{[12]}]_1Li_6^{[4]}[U^{[6]}O_6]$ (*96*) the structure is ambivalent. Apparently the nearly perfect grouping $[UO_6]$ plays the dominant role. Probably the same grouping occurs in $K_2Li_4[UO_6]$ (*97*). From a different point of view it is the large vacancy, (see Figs. 4 and 13 and Table XXV) of C.N. 12 which is the most interesting part of the constitution. One asks immediately whether or not this huge hole could be filled. Up to now all our attempts to reduce with metallic K so as to form $KLi_6[UO_6]$ have failed.

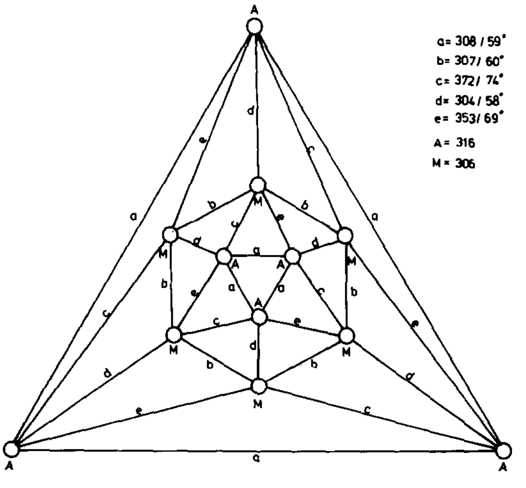


FIG. 13. Schlegel projection of the CP of vacancy $[L^{12}]$ in α-$Li_6[UO_6]$. Distances of corners from L, lengths of edges of the CP (in pm), and angles O—L—O (degrees) are indicated.

Nevertheless it is the vacancy which forms a LO_{12} unit surrounded in a manner best expressed by $[(LO_{12})Li_{12}U_2] = Li_6UO_6$; these nearly perfect icosahedral entities form a densest packing of spheres.

XVI. New Oxoiridates

At the same time we investigated new oxoiridates such as $Li_8[IrO_6]$ (*98*) which belong to the Li_8SnO_6 type of structure already mentioned. In addition we have prepared new oxoiridates: first, $K_4[IrO_4]$ (*99*), then $Rb_4[IrO_4]$ (*100*) and most recently $Rb_2K_2[IrO_4]$ (*100*). Surprisingly all these iridates are characterized by a square group $[IrO_4]$; yet they do not show the low spin state of the d^5 system of electrons ($\mu = 2.9$ μ_B, $\theta = -2$ K at 300–10 K). This matter has to be studied further in more detail.

In hunting for compounds like $K_2Li_2[IrO_4]$ or $K_2Li_4[IrO_5]$ we incidentally obtained dark single crystals of $KLi_6[Ir^VO_6]$ (*101*). This is (see Table XVI) in correspondence with the still sought-after $KLi_6[UO_6]$. MAPLE of $KLi_6[IrO_6]$ fits excellently with MAPLE of $K[IrO_3]$ (*102*), obtained as the first iridate(V) years ago (see Table XXVII, and Figs. 14 and 15. (MAPLE: MAdelung Part of Lattice Energy.)

XVI. Tightrope Walking

Oxotungstates of the alkali metals are mainly "poor in cations," like $K_2[WO_4]$

TABLE XXV

MOTIFS OF MUTUAL ADJUNCTION OF Li_6UO_6

	6 O^{2-}	C.N.
1 U^{6a+}	6/1 (209)	6
6 Li^+	1/1 + 1/1 + 1/1 + 1/1 (194) (196) (200) (202)	4
1 □	6/1 + 6/1 (306) (316)	(12)
C.N.	5(+2)	

TABLE XXVI

$KLi_6\,[IrO_6]$: MOTIFS OF MUTUAL ADJUNCTION

	O^{2-}	C.N.
Ir^{5+}	6/1 (200)	6
K^+	6/1 + 6/1 (295) (306)	12
Li^+	2/2 + 2/2 (193) (195)	4

(*103*) or at best "neutral" in this respect, like $K_4[WO_5]$ (*9*). This oxide and its companions such as $Rb_4[WO_5]$ (*9*) as well as $K_4[MoO_5]$ (*9*) contain trigonal bipyramids $[WO_5]$. But we have the ENSTATITE SYNDROME and thus, a very complicated structure, as already mentioned above. The formation of a simple derivative of the NaCl type is obviously hindered by the large size of K^+/Rb^+. What can we do to rush from the "tight rope" of such an unhealthy complicated structure on the simpler base of NaCl derivatives?

It is sufficient to replace artfully smaller by larger M^{+6}, or larger by smaller A^+. Thus, K_4UO_5 (*104*) on one hand, and Na_4WO_5, Li_4MoO_5, and Li_4WO_5 (*105*) on the other, are ordered derivatives of MgO (*106*). But we do not yet know what happens in the case of Rb_4UO_5 (*104*). In all these compounds to which Niggli's formula $[MO_{4/1}O_{2/2}]$ applies (with M = U, W, Mo, or Te) there exist several different possibilities of structural realization within the NaCl type structure: (a) we could encounter corner-connected infinite chains of octahedra with either *cis* or *trans* (or an alternating motif of) connections; (b) another possibility involves formation of dimeric groups such as $[O_4MO_2MO_4]$ with M in the M^{VI} state. In fact in all cases known so far, even

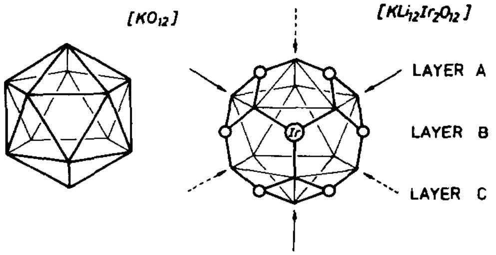


FIG. 14. The icosahedron KO_{12} in $KLi_6[IrO_6]$ (left) and corresponding next nearest neighbors (right). See Fig. 15 for stacking of layers.

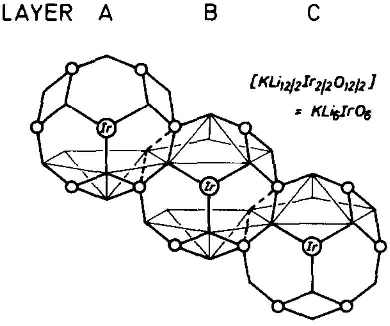


FIG. 15. Stacking of icosahedra KO_{12} and the corresponding next nearest neighbors ABCA. . . of c.c.p. in $KLi_6[IrO_6]$.

TABLE XXVII

MADELUNG PART OF LATTICE ENERGY, MAPLE OF KLi_6IrO_6 (kcal · mol^{-1})

		Binary	Quaternary	Δ	$\Sigma\Delta^c$
Ir^{5+}	1×	2906.7^a	2832.9	−73.8	−73.8
K^+	$\frac{1}{3}$×	150.5^a	108.3	−42.2	
	$\frac{2}{3}$×	143.8^a		−35.5	−37.7
Li^+	6×	146.2^b	176.3	+30.1	+180.6
O^{2-}	3×	543.5^b	567.8	+24.3	
	1×	597.7^a		−29.9	−42.2
	2×	610.4^a		−42.6	
		7379.0	7405.9		+26.9 = +0.36%

[a] From $KIrO_3$.

[b] From Li_2O.

[c] Δ + quaternary − binary: MAPLE(KLi_6IrO_6) − MAPLE($KIrO_3$) − 3 · MAPLE(Li_2O).

TABLE XXVIII

$Na_6Li_2[W_2O_{10}]$ MOTIFS OF MUTUAL ADJUNCTION

	$\overset{1}{O}$	$\overset{2}{O}$	$\overset{3}{O}$	$\overset{4}{O}$	$\overset{5}{O}$	C.N.
$\overset{1}{Na}$	1/1 (237.4)	—	1/1 + 1/1 (234.1) (238.2)	1/1 (230.9)	1/1 + 1/1 (235.8) (236.5)	6
$\overset{2}{Na}$	1/1 (231.7)	1/1 + 1/1 (225.8) (228.4)	1/1 (266.8)	1/1 + 1/1 (230.9) (252.7)	—	6
$\overset{3}{Na}$	1/1 + 1/1 (239.2) (252.6)	1/1 + 1/1 (237.4) (239.5)	—	1/1 (232.1)	1/1 (250.4)	6
Li	1/1 (216.5)	(1/1) (323.0)	1/1 (210.9)	1/1 (201.4)	1/1 + 1/1 (205.5) (227.1)	5(+1)
W	1/1 (184.9)	1/1 (180.9)	1/1 + 1/1 (202.4) (216.4)	1/1 (190.8)	1/1 (191.6)	6
C.N.	6	5(+1)	6	6	6	

TABLE XXIX

$Cs_2K_2[TeO_5]$: MOTIFS OF MUTUAL ADJUNCTION

	2$\overset{1}{O}$	2$\overset{2}{O}$	1$\overset{3}{O}$	C.N.	MEFIR
$\overset{1}{Cs}$	2/1 313	2/1 286	2/2 302	6	157 pm
$\overset{2}{Cs}$	4/2 320	4/2 339	—	8	189 pm
Te	2/1 188	2/1 194	1/1 188	5	50 pm
2K	2/2 271	1/1 2/2 265 284	1/2 277	6	134 pm
C.N.	6	7	5		
MEFIR	139 pm	141 pm	142 pm		

TABLE XXX

$K_3Li_3[TeO_6]$: MOTIFS OF MUTUAL ADJUNCTION

	1$\overset{1}{O}$	1$\overset{2}{O}$	2$\overset{3}{O}$	2$\overset{4}{O}$	C.N.	MEFIR
1 Te	1/1 193	1/1 194	2/1 194	2/1 195	6	54 pm
1 $\overset{1}{K}$	—	1/1 273	2/1 273	2/1 + 2/1 302 315	7	144 pm
1 $\overset{2}{K}$	1/1 270	—	2/1 285	2/1 + 2/1 259 283	7	131 pm
1 $\overset{3}{K}$	1/1 256	1/1 270	2/1 + 2/1 280 283	—	6	129 pm
2 $\overset{1}{Li}$	1/2 194	1/2 194	1/1 205	1/1 199	4	58 pm
1 $\overset{2}{Li}$	—	—	2/1 210	2/1 205	4	67 pm
C.N.	5	5	7	7		
MEFIR	136	138	142	141		

with Na_3LiWO_5 (*107*), it is the latter motif that is encountered. Li^+ of course avoids C.N. 6 and is only occasionally associated with C.N. 5 (see Table XXVIII and Fig. 16).

We call attention to the near relationship that is found between elements of the same "main" and "sub" groups of elements. So $Cs_2K_2[TeO_5]$ (*108*) (TABLE XXIX) and $K_2Na_2[TeO_5]$ (*108*) correspond to $K_4[WO_5]$ in having trigonal bipyramids. Incidentally, $K_4Na_2[TeO_6]$ or $K_3Li_3[TeO_6]$ (*108*) contain "isolated" octahedra (see Table XXX) with striking differences in the C.N. of the O^{2-}, although a well-balanced MMA is possible (Table XXXI).

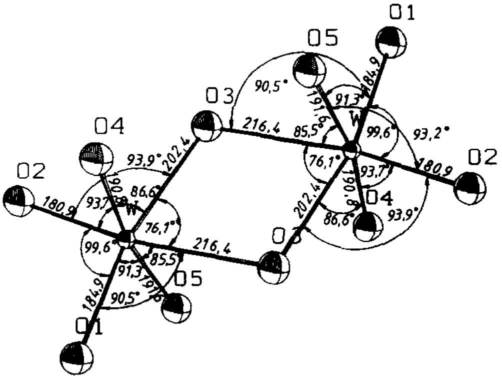


FIG. 16. Structure of the dimeric anion $[O_4WO_2WO_4]$ in $NaLi_3WO_5$.

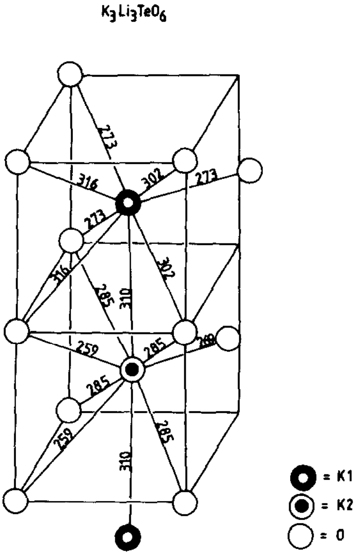


FIG. 17. Structure showing d(K—O) and d(K—K) (pm) in $K_3Li_3TeO_6$.

One should examine the interatomic distances realized with $K_3Li_3[TeO_6]$ to understand how ill-defined the term C.N. really is used as commonly (see Fig. 17).

XVIII. New Families of Oxides: $A_m[(TO)_n]$ and $A_m[(TO)_n(TO_2)_p]$

All zeolites belong to the series $A_m[(TO_2)_p]$, and all are typified by characteristic 3-dimensional frameworks $[(TO_2)_p]$. With the recently discovered members of a new series $A_m[(TO)_n]$ the situation is different. At present with $m = 1$ only KNaO (*109*) a member of the PbClF type ($n = 1$), and Na $[LiZnO_2]$ (*54*) are known ($n = 2$), where, surprisingly, all tetrahedral sites between layers A and B and all octahedral sites between B and A of a distorted hexagonal closed packing of O^{2-} are occupied alternatively. KLi_3SiO_4 (*110*), which then corresponds to $K[Li_3SiO_4]$, exhibits a more complicated structure, showing a distorted body-centered cubic packing of K^+ and O^{2-} with Li^+ and Si^{4+} in its pseudo-tetrahedral sites. The C.N. of K^+ is 8—the CPs, irregular cubes $KO_{8/2}$, form chains. Similar chains have also been dis-

TABLE XXXI

$K_3Li_3TeO_6$: POSSIBLE MOTIFS OF MUTUAL ADJUNCTION

	101	102	103	104	105	106	C.N.
1 Te	1/1	1/1	1/1	1/1	1/1	1/1	6
3 K	1/3	1/3	1/3	1/3	1/3	1/3	6
1 Li1	1/1	1/1	1/1	1/1	—	—	4
1 Li2	1/1	1/1	—	—	1/1	1/1	4
1 Li3	—	—	1/1	1/1	1/1	1/1	4
C.N.	6	6	6	6	6	6	

TABLE XXXII

OXIDES $A\{(TO)_4\}$: PREPARATION OF $NaLi_3[SiO_4]$

$$1.2\ NaO_{0.45} + 3.2\ LiO_{0.50} + 1.0\ SiO_2 \xrightarrow[1d \rightarrow n \cdot d]{Ni/300° \rightarrow 1000°C}$$

Very hard single crystals colorless, transparent

$I\ 4_1/a$ with $a = 1078.4(1)$ pm
$c = 1263.3(1)$ pm

1031 out of 1287 I_0 (hkl)
$R = 8.4\%$, $R_w = 6.2\%$

TABLE XXXIII

$NaLi_3SiO_4$: MOTIFS OF MUTUAL ADJUNCTION

	1(O1)	1(O2)	1(O3)	1(O4)	ECoN	MEFIR
1 Si	1/1 162	1/1 162	1/1 162	1/1 163	4.0	22 pm
1 Na	1/1 + 1/1 249 273	1/1 244	1/1 + (1/1) 250 (305)	1/1 + 1/1 248 260	5.9	112 pm
1(Li1)	1/1 + 1/1 193 196	—	1/1 + 1/1 196 208	—	3.9	57 pm
1(Li2)	—	1/1 + 1/1 192 216	—	1/1 + 1/1 184 196	3.5	52 pm
1(Li3)	1/1 193	1/1 218	1/1 200	1/1 198	3.9	60 pm
ECoN	5.5	4.7	5.9	5.1		
MEFIR	139 pm	137 pm	139 pm	137 pm		

TABLE XXXIV

OXIDES $A_2\{(TO)_2(T'O_2)\}$: PREPARATION OF $Rb_2Li_2[SiO_4]$

$$2.5\ RbP_{0.48} + 2.4\ LiO_{0.50} + 1.0\ SiO_2 \xrightarrow[1d \overset{\circ}{\rightarrow} 10d]{Ni/300°C \overset{\circ}{\rightarrow} 800°C}$$

"Soft" single crystals colorless, transparent

$P\bar{1}$ with

$a = 897.9(1)$ pm	$\alpha = 94.0(1)°$
$b = 564.7(1)$ pm	$\beta = 111.2(1)°$
$c = 547.0(1)$ pm	$\gamma = 93.8(1)°$

2018 out of 2457 I_0 (*hkl*)
$R = 8.4\%$, $R_w = 6.4\%$

TABLE XXXV

QUATERNARY OXIDES

Here, e.g.,
$Rb_2Li_2[SiO_4] \triangleq Rb_2\ \{(LiO)_2\ (SiO_2)_1\}$
$\triangleq A_x\{(TO)_m(TO_2)_n\}$
act in accordance with the motto: My children thrash your children

covered in $NaLi_3SiO_4$ (see Tables XXXII and XXXIII) (*111*).

$Rb_2Li_2SiO_4$ (*112*) is the only known member of the series $A_m[(TO)_n(TO_2)_p]$ which formally connects the series above mentioned with the zeolites (see Tables XXXIV and XXXV). Whether or not still unknown members of this series exist with zeolite-like congruent structural behavior is uncertain. Since with $Rb_2Li_2SiO_4$ the two Rb^+ are very unlike with respect to their C.N., (see Table XXXVI), the synthesis of new oxides like $CsRbLi_2SiO_4$ or $RbKLi_2SiO_4$ seems both necessary and interesting.

XIX. The First Cluster with Indium: $[In_5]$

The crystal structure of intermetallic compounds such as NaTl is easily understandable on the basis of the ZINTL-KLEMM-concept. With respect to the relatively broad range of homogeneity of, e.g., NaTl, this concept serves only as a rough guide. To determine whether the concept is more specifically useful, we oxidized e.g., NaIn slowly (see Table XXXVII and Figs. 18 and 19) and obtained $Na_{24}[In_5]O_{15}$ (*113*) as single crystals. At the moment the inner constitution of the group $[In_5]^{6+}$ as well as the reasons for the short bond lengths *d*(In—In) and the diamagnetism are not understood.

TABLE XXXVI

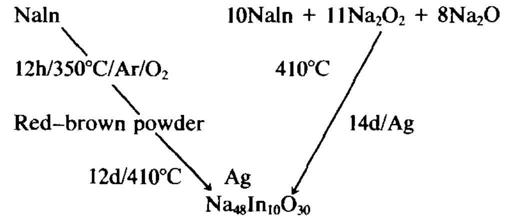
$Rb_2Li_2SiO_4$ MOTIFS OF MUTUAL ADJUNCTION

	1(O1)	1(O2)	1(O3)	1(O4)	ECoN	MEFIR
1 Si	1/1 166	1/1 165	1/1 165	1/1 161	4.0	24 pm
1(Rb1)	1/1 + 1/1 307 307	1/1 + 1/1 319 321	1/1 + 1/1 295 343	1/1 + 1/1 300 321	8.1	171 pm
1(Rb2)	—	1/1 + 1/1 279 305	—	1/1 + 1/1 + 1/1 + 1/1 275 284 294 328	5.6	148 pm
1(Li1)	1/1 + 1/1 197 200	1/1 198	1/1 198	—	4.0	58 pm
1(Li2)	1/1 219	1/1 185	1/1 + 1/1 193 194	—	3.4	52 pm
ECoN	6.5	6.7	6.0	6.3		
MEFIR	142 pm	140 pm	140 pm	139 pm		

TABLE XXXVII

THE FIRST CLUSTER $[In_5]$

Preparation by reduced oxidation of NaIn



Dark red cubic single crystals
Space group = $I\bar{4}3m$
$304 I_0$(hKL)
$R = 6.01\%$

XX. Oxidation of Intermetallic Compounds

Surprisingly, little is known about the oxidation of intermetallic compounds, at least those of the alkali, alkaline earth and the rare earth metals:

Long ago with NaTl we obtained β-$NaTlO_2$ (*114*), as a disordered variant of NaCl type. This indicates that in conformity with Ostwald's rule this is a HT-form of $NaTlO_2$. In case of CsAu we obtained $CsAuO = Cs_4[Au_4O_4]$ (*115*), a member of the $K_4[Ag_4O_4]$ family of oxides (see above) and for years the only known oxoaurate(I) (see below).

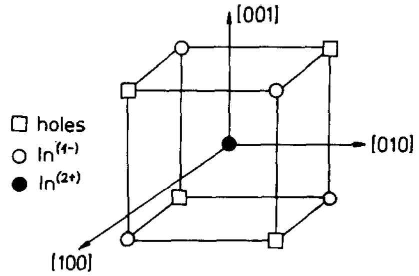


FIG. 19. Illustration of the arrangement of the In atoms in the In_5 cations of the $Na_{48}(In_5)_2O_{30}$ structure. $d(\text{In–In})_{\text{cluster}} = 274$ pm; $d(\text{In–In})_{\text{metal}} = 4 \times 325$ pm and 8×337 pm.

Starting with KSn we studied such reactions during the past 4 years in detail. With KSn and RbSn we obtained new modifications (*116*) of $K_2Sn_2O_3$ and $Rb_2Sn_2O_3$ (*117*) which are isostructural to $K_2Pb_2O_3$ (*118*) (see Figs. 20 and 21). Here we have corresponding to $KPbO_{3/2}[L]_{3/2}$ a perovskite where half of the O^{2-} is substituted for by ordered vacancies such that the framework

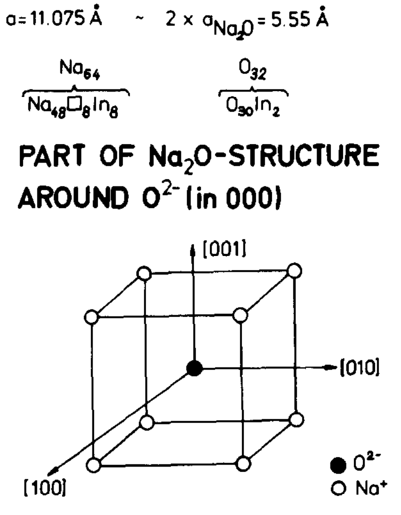


FIG. 18. Some structural features of $Na_{48}(In_5)_2O_{30}$.

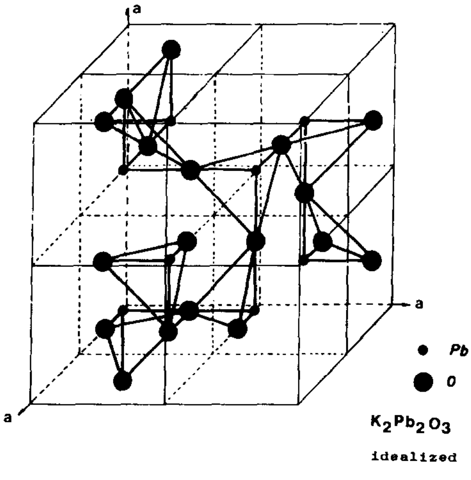


FIG. 20. Structure of $K_2Pb_2O_3$.

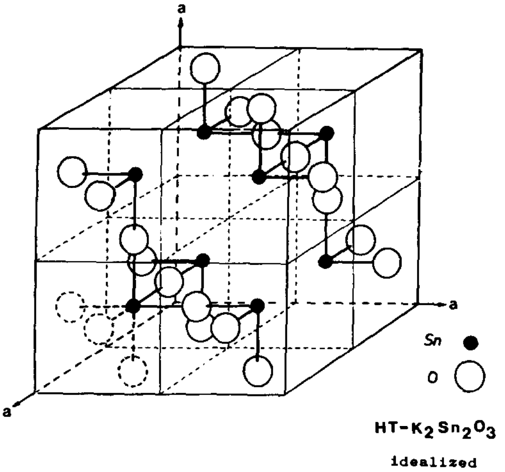


FIG. 21. Structure of HT—$K_2Sn_2O_3$ (idealized).

[$PbO_{3/2}$] still remains three dimensional. In normal modifications of stannates(II) including $Cs_2Sn_2O_3$ (*119*) the ordered vacancies generate a layer structure ($^2_\infty[SnO_{3/2}]$). With KGe we obtained the first oxogermanate(II), $K_2Ge_2O_3$ (*120*) (see Fig. 22), adopting the $K_2Sn_2O_3$ type of structure. In this case, however, only impure powder samples were obtained, the main impurity being $K_6Ge_2O_7$ (*121*).

Different methods for oxidizing, e.g., NaTl are collected in Table XXXVIII. Attention here is drawn to Na_3TlO_2 (*122*); Table XXXIX shows the MMA. There are two types of vacancies within the structure. One sort is such that—if it were occupied—it would increase the C.N. of both Na^+ and Tl^+ to be 6. The other one could be a location for the "Lone Pair of Electrons" (LP) of Tl^+, if such entities actually occur.

The structure is best described by starting with the CP of the O^{2-}. Both of them are "good octahedra" (see Figs. 23, 24, 25). This provides the start for the derivation of the whole structure using the two SCHLEGEL-diagrams of the CP of the anions. The full treatment is given elsewhere (*122*). With NaAu, we obtained by oxidation with Na_2O_2 and K_2O_2 single crystals of $KNa_2[AuO_2]$ (*123*), the first oxoaurate(I) with the XeF_2-like group [O—Au—O], d(Au—O) = 201 pm (Table XL). Surprisingly this oxide differs in crystal structure from $KNa_2[CuO_2]$ and $KNa_2[AgO_2]$ mentioned before.

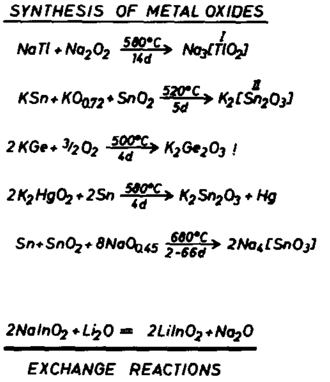


FIG. 22. Results of the oxidation of intermetallic compounds.

XXI. The Mechanism of Formation of Metal Oxides: Intermediates

For metal oxides "rich in cations" nearly nothing is known about what happens during formation.

In the case of $LiInO_2$ we investigated long ago (by the Debye–Scherrer-method

TABLE XXXVIII

OXIDATION OF INTERMETALLIC PHASES

(1) $NaTl \xrightarrow[580°C/Ag/10d]{1Na_2O_2} Na_3TlO_2$

(2) $NaTl \xrightarrow[600°C/Ag/14d]{1Li_2O_2}$ "β-NaTlO"

(3) $NaTl \xrightarrow[500°C/Ag/14d]{1HgO} \alpha$-NaTlO

(4) $4NaTl \xrightarrow[580°C/Ag/14d]{3Na_2O_2 + 2Rb_2O} Rb_4Na_4Tl_4O_6$

(5) $NaTl \xrightarrow[580°C/Ag/14d]{2Na_2O_2} Na_5TlO_4$

TABLE XXXIX

Na_3TlO_2: MOTIFS OF MUTUAL ADJUNCTION

	1O(1)	1O(2)	C.N.	ECoN[a] (pm)	MEFIR (pm)	LI	LII	C.N.[e]	(LP)	C.N.[f]
1 Tl	2/2 (234)	1/1 (231)	3	2.9	94	2/2 (243)	1/1 (224)	3 + 3	1/1 (80)	3 + 1
2 Na(1)	1/2 (233)	1/2 + 1/2 (235) (236)	3	2.9	95	1/2 (233)	2/4 (235)	3 + 3	1/2 (273)	3 + 1
1 Na(2)	2/2 (234)	1/1 (230)	3	2.9	93	2/2 (231)	1/1 (248)	3 + 3	1/1 (273)	3 + 1
C.N.	6	6				6	6		4	
						O(1)	O(2)			
ECoN[b]	5.9	5.9			MEFIR[b]	141	140			
ECoN[c]	7.5	6.6			MEFIR[c]	144	142			
ECoN[d]	4.5	3.6			MEFIR[d]	170	176			

Note. Starting values of ionic radii: for "calibration" $R(O^{2-}) = 140$ pm and following the ECoN conception from the weighted mean distances $\bar{d}(Tl^+) = 94$ pm, $\bar{d}[Na(1)^+] = 95$ pm, $\bar{d}[Na(2)^+] = 93$ pm.

[a] ECoN ($M/\Sigma O$).

[b] ECoN ($O/\Sigma M$).

[c] ECoN [$O/(M + O)$].

[d] ECoN (O/O).

[e] CN(O + L).

[f] CN(O + LP).

only) what happens when mixtures of Li_2O and In_2O_3 are heated with or without additives (like CoO) under O_2: obviously intermediates were formed (*124*). One of these was characterized by a cubic unit cell of the NaCl type with doubled *a* axis, for which $Z = 16$ instead of $Z = 2$ as in $LiInO_2$. This raises the question as to what are the first steps. Does Li_2O attack In_2O_3 by diffusion? Is LiOH, formed from traces of moisture, always present?

With β-$LiRhO_2$, we recently encountered

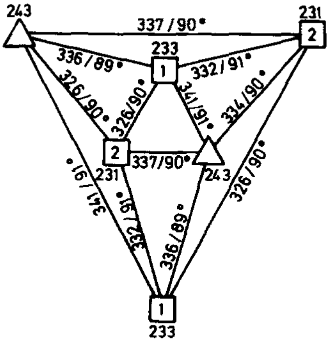


FIG. 23. Schlegel diagram of the CP of $\overset{1}{O}{}^{2-}$ in Na_3TlO_2. Distances of corners from O_1, lengths of edges (pm) and angles M—O—M show that the CP is a "good" octahedron. Tl^+ (△), Na^+ (□).

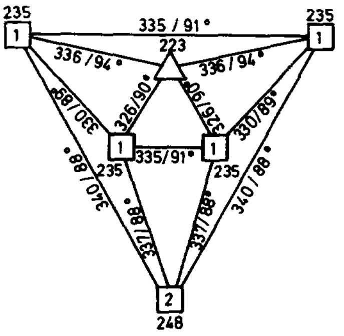


FIG. 24. Schlegel diagram of the CP of $\overset{2}{O}{}^{2-}$ in Na_3TlO_2. Distances of corners from O_2, lengths of edges (pm), and angles M—O—M show that the CP is a "good" octahedron. Tl^+ (△), Na^+ (□).

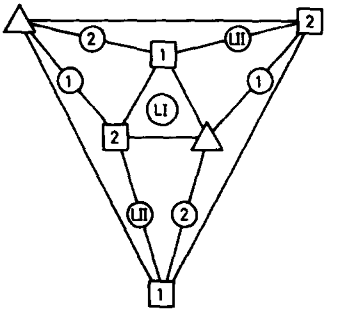


FIG. 25. Schlegel diagram of the CP of vacancy L in Na_3TlO_2. Tl^+ (△), Na^+ (□).

an example of such a NaCl unit cell with superstructure. β-$LiRhO_2$ (*125*) was prepared according to the reaction

$$2.9Li_2O + 1.4Na_2O + 1Rh_2O_3 \xrightarrow[18\ d]{950°C/Pd} 2\beta\text{-}LiRhO_2 + \ldots$$

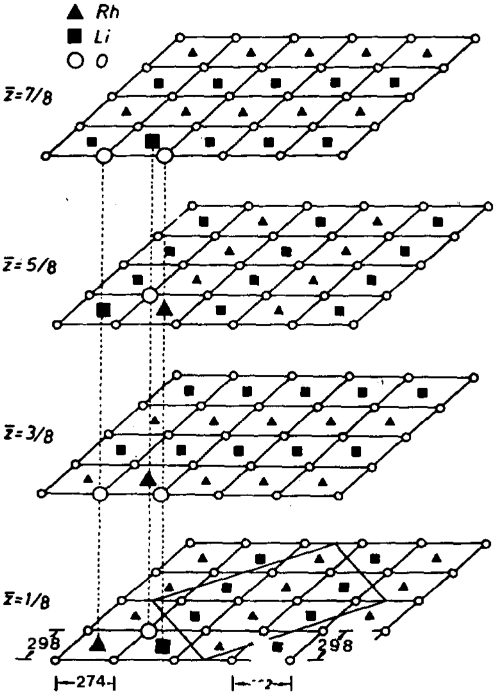


FIG. 26. Sequence of NaCl-like layers in cubic β-$LiRhO_2$. d(Rh–O) = 202.4 pm (6×); d(Li–O) = 219.2 pm (6×).

TABLE XL

$KNa_2[AuO_2]$: MOTIFS OF MUTUAL ADJUNCTION

	2O	C.N.	ECoN[a] (pm)	MEFIR[a] (pm)
1 Au	2/1 (201)	2	2.0	61
2 Na	1/1 + 2/2 (235) (229)	3	3.0	93
1 K	4/2 (285)	4	4.0	142
C.N.	6			O
ECoN[b]	6.0		MEFIR[b]	141
ECoN[c]	6.0		MEFIR[c]	141

Crystallographic data
Space group $Pnnm - D_{2h}^{12}$, $Z = 2$
Lattice constants (Guinier–Simon data, pm):
a = 1025.6 (3)
b = 547.2 (2)
c = 399.98(9)
R = 6.2% and R_w = 6.7%

Note. Starting values of ionic radii: for "calibration" $R(O^{2-})$ = 140 pm and following the ECoN conception from the weighted mean distances $\bar{d}(Au^+)$ = 61 pm, $\bar{d}(Na^+)$ = 93 pm, $\bar{d}(K^+)$ = 142 pm.

[a] ECoN ($M/\Sigma O$).

[b] ECoN ($O/\Sigma M$).

[c] ECoN [$O/\Sigma(M + O)$].

In this process we obtained black single crystals [$F4_132$, a = 841.27(6) pm (Guinier photographs, Cu$K\alpha$); R = 9.1 and R_w = 5.46% for 100 out of 109 I_0 (hkl), four circle diffractometer PW1100, Ag$K\alpha$] (see Table XLI and Fig. 26).

TABLE XLI

SUPERSTRUCTURES OF NaCl VARIANTS

β-$LiRhO_2$

$$2.91Li_2O + 1.45Na_2O + Rh_2O_3 \xrightarrow[18d]{950°C/Pd} \beta\text{-}LiRhO_2 \text{ (black)}$$

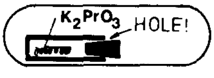
$F4_132$	100 of 109 I_0 (hkl)
a = 841.27(6) pm	R = 9.10%
	R_w = 5.46%
	(Ag$K\alpha$)

TABLE XLII

SYNTHESIS OF SINGLE CRYSTALS OF Pr_2O_3

Remember:

Binary oxides are the noms of all oxides; e.g., for the La_2O_3 type, Pauling created a proposal in 1928. We confirmed this in 1985:



$$K_2PrO_3 \xrightarrow[1000°C]{Ni,\ 14d} Pr_2O_3$$

XXII. The Decomposition of Metal Oxides

Nearly all of the metal oxides mentioned here are immediately decomposed by moisture. Once again nearly nothing is known on the mechanism of decomposition or the nature of the final product.

In $RbAlO_2$ we studied the reaction

$$2\ RbAlO_{2,solid} + 7H_2\ O_{gas} = Rb_2[(H_2O)_2(OH)_3Al—O—Al(OH)_3(H_2O)_2]_{solid}$$

and found that the reaction stops with the indicated compound, not with $Rb[Al(OH)_4]$ or $Rb[Al(OH)_4(OH_2)_2]$ as we anticipated (*126*).

Little is known of the reaction with other gases. In the case of F_2, we found with Na_2PbO_3:

$$Na_2PbO_{3,solid} + F_{2gas} = 2\ NaF_{solid} + \text{“}PbO_2\text{”}_{,solid}$$

as a first step. Since on heating we also observed the reaction

$$2\ Na_2PbO_{3,solid} + Na_2PbF_{6,solid} = 6\ NaF_{solid} + 3\ \text{“}PbO_2\text{”}_{,solid}$$

already at 320°C (*127*) the first step appears to be a step of equilibrium. Further heating then leads to complete "fluorination" and the formation of $Na_2PbF_{6,solid}$ from $Na_2PbO_{3,solid}$. The *thermal decomposition* of such metal oxides using a semiclosed system turns out to be very useful. In the case of, e.g., $K_4[SiO_4]$ (*128*) we obtained single crystals of $K_6[Si_2O_7]$ (*129*).

On heating K_2PrO_3 (*130*) in small Ni cylinders with a small hole [1000°C, 14 days, quartz tube, Ar] we obtained for the first time, at relatively "low" temperature, beautiful single crystals of Pr_2O_3 (Table XLII) and confirmed Pauling's proposal for its structure (*131*). Single crystals of Ce_2O_3 were obtained (*132*) in a similar manner.

The differences in distances *d*(Pr—O) are rather large; no simple explanation of this feature exists. Other examples from oxoplumbates are collected in Table XLIII (*133*).

XXIII. Mixed Valence Oxides with Lead

It has been asserted that a *black* $KPbO_2$ exists (*134, 135*). As shown by our investigations this is a high temperature modification (*133*) of unknown structure and possibly slightly different in composition from "$KPbO_2$."

We obtained orange-red crystals of the low temperature form, from which we determined the constitution shown in Table XLIV and Figs. 27–29 (*136*). While Pb^{II} is directly and wholly attached to rutile-like chains of octahedra surrounding Pb^{IV}, the situation with $Rb_2Pb_4O_7$ (*137*) is completely different.

TABLE XLIII

THERMAL DECOMPOSITION

(1) $K_2Li_6[Pb_2O_8] \xrightarrow[690°C]{Ag/100d} TT—Li_2PbO_3$

(2) "$K_2Pb_2O_5$" $\xrightarrow[700°C]{Ag/30d} \beta—K_2PbO_3$

(3) $Cs_2Li_{14}[Pb_3O_{14}] \xrightarrow[Ag\text{-}cylinder]{650°C} 3Li_4[PbO_4]$
(Single crystals)

(4) $K_2Li_6[Pb_2O_8] \xrightarrow[Ag\text{-}cylinder]{690°C} TT—Li_2PbO_3$
(Single crystals)

TABLE XLIVa

MIXED VALENCE OXOPLUMBATES $KPbO_2$

(1) Preparation of α-$KPbO_2$

(a) $K_2O_2 + 2PbO_{red} \xrightarrow[560°C]{20d} \dfrac{2KPbO_2}{\text{orange–red}}$

(b) $K_2PbO_3 + PbO_{red} \xrightarrow[560°C]{10d} 2KPbO_2$

(2) Lattice-constants of α-$KPbO_2$

$a = 12.96_4$ Å $\alpha = 117.9_6$

$b = 7.52_9$ Å $\beta = 106.1_7$

$c = 6.97_0$ Å $\gamma = 93.4_7$

(3) Reversible transformation

α-$KPbO_2$ $\xrightleftharpoons{\sim 650°C}$ "β-$KPbO_2$"

Orange–red Black–violet

(4) Structure determination

3950 I_0 (*hkl*) (Four-circle diffractometer)

Ag*K*α radiation

$R = 8.01\%$, $R_w = 6.95\%$ for 2974 I_0 (*hkl*)

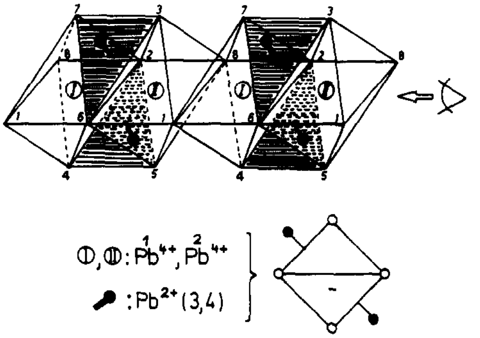


FIG. 27. Structure of α-$KPbO_2$ showing attachment of Pb^{2+} to rutile-like chains $[Pb^4O_{4/2}O_{2/1}] \triangleq [PbO_4]$ in $K_2Pb^{2+}[PbO_4 \triangleq KPbO_2$.

Here Pb^{II} acts as a connecting bridge between different chains of $[Pb^{IV}O_6]$-octahedra. In fact these are double-chains of the type found in β-Ga_2O_3 (see Fig. 30).

We already mentioned the curiosity, that $Na_4[PbO_4]$ is the missing link within the series $A_4[PbO_4]$. There are other peculiarities in sodium plumbates(II): there is still no evidence for $Na_4[Pb^{II}O_3]$, although $K_4[Pb^{II}O_3]$ is well known (*138*).

Recently we obtained orange–red crystals of $KNa_7Pb_2O_7 = KNa_7[Pb^{II}O_3][Pb^{IV}O_4]$ (*139*) (see Table XLV).

The structure also shows all the attributes of an oxoplumbate(II) like $K_4[Pb^{II}O_3]$

TABLE XLIVb

MOTIFS OF MUTUAL ADJUNCTION IN α-$KPbO_2 = K_2Pb_2O_4$[a]

	2O(1)	2O(2)	2O(3)	2O(4)	2O(5)	2O(6)	2O(7)	2O(8)	C.N.	ECoN[b]	MEFIR
2 Pb(1)	1/1 (219)	1/1 (236)	—	1/1 (210)	—	1/1 (240)	1/1 (214)	1/1 (228)	6	5.3_3	79
2 Pb(2)	1/1 (215)	1/1 (236)	1/1 (210)	—	1/1 (212)	1/1 (240)	—	1/1 (227)	6	5.3_0	78
2 Pb(3)	—	—	1/1 (225)	—	—	1/1 (225)	1/1 (218)	—	3	2.9_7	82
2 Pb(4)	—	1/1 (223)	—	1/1 (220)	1/1 (226)	—	—	—	3	2.9_9	84
2 K(1)	1/1 (273)	1/1 (272)	1/1 (273)	1/1 (277)	1/1 (276)	—	1/1 (269)	—	6	5.9_8	133
2 K(2)	—	1/1 (291)	—	1/1 (273)	1/1 + 1/1 (262) (306)	—	—	1/1 + 1/1 (268) (278)	6	5.3_0	134
2 K(3)	—	—	1/1 (258)	1/1 (274)	1/1 (297)	1/1 (284)	1/1 (280)	1/1 (278)	6	5.4_6	133
2 K(4)	1/1 + 1/1 (271) (283)	—	1/1 (277)	—	—	1/1 (273)	1/1 + 1/1 (291) (310)	—	6	5.5_1	141
C.N.	5	5	5	5	6	5	6	5			
ECoN[c]	4.9_4	4.6_8	4.8_7	4.9_2	5.1_6	4.4_4	5.6_0	4.8_8			
MEFIR	138	144	137	138	139	143	141	142			

Note. The starting values of the ionic radii were determined basing on the ECoN concept: 140 (standard: $R(O^{2-})$) is subtracted from $\bar{d}$(Me—O).

[a] Distances and MEFIR in pm, SD: 0–2 pm.

[b] ECoN (Me/ΣO).

[c] ECoN (O/ΣMe).

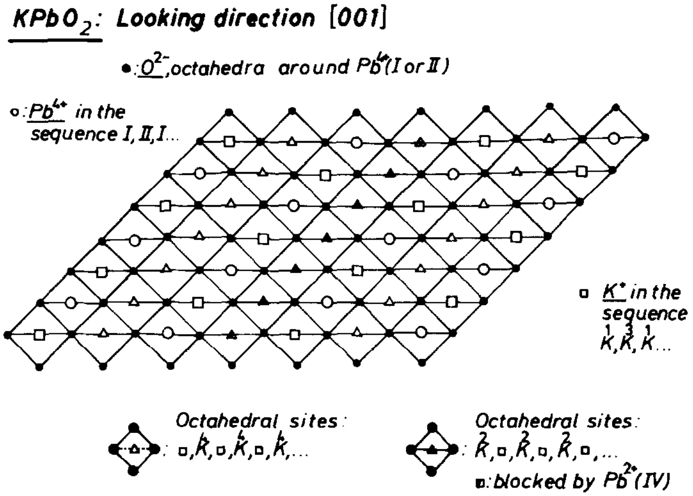


FIG. 28. Connection of octahedral CP of K^+ and Pb^{4+} in $K_2Pb^{2+}[Pb^{4+}O_4]$.

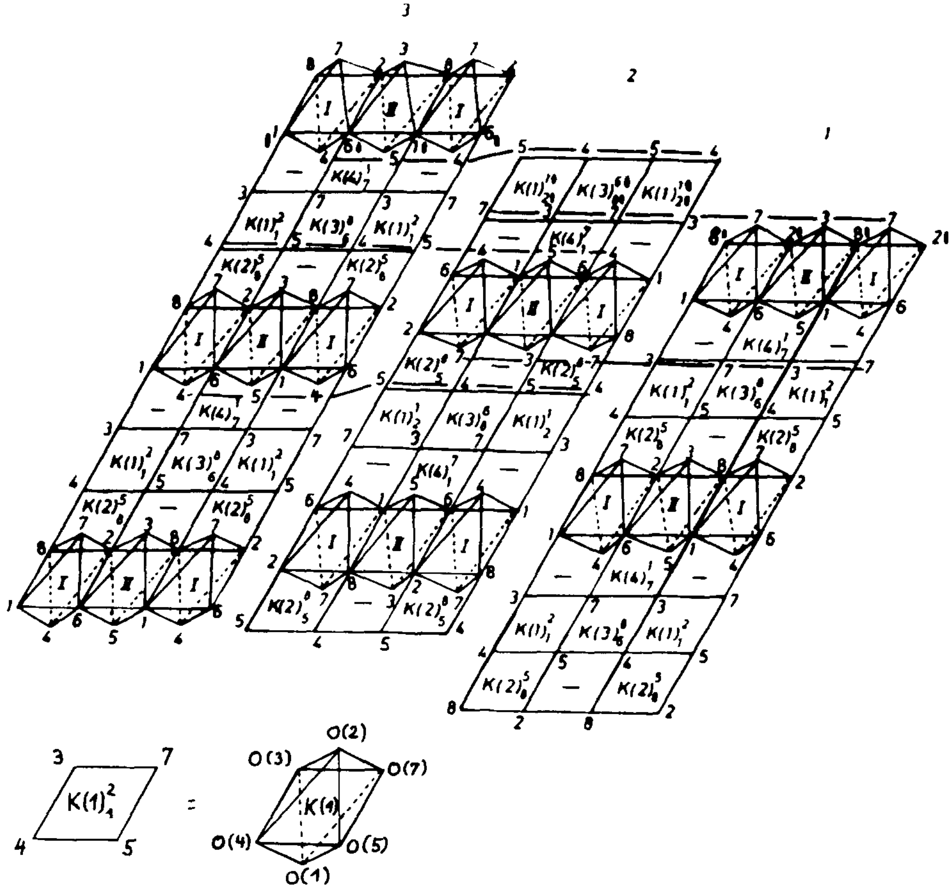


FIG. 29. $KPbO_2$: Stacking of layers of connected octahedra (CP of Pb^{4+} and K^+) as viewed on (001) planes. I = Pb(1), II = Pb(2).

TABLE XLV

MOTIFS OF MUTUAL ADJUNCTION IN $KNa_7Pb_2O_7 = KNa_7[PbO_3][PbO_4]^a$

	4O(1)	4O(2)	4O(3)	4O(4)	4O(5)	4O(6)	4O(7)	C.N.	ECoN[b]	MEFIR
4 Pb(1)	—	—	—	—	1/1 (221)	1/1 (216)	1/1 (219)	3	2.9_9	79
4 Pb(2)	1/1 (207)	1/1 (210)	1/1 (210)	1/1 (206)	—	—	—	4	3.9_9	68
4 K	1/1 + 1/1 + 1/1 (275) (297) (301)	—	1/1 + 1/1 (273) (292)	1/1 (280)	—	—	—	6	5.6_2	143
4 Na(1)	—	—	—	—	—	1/1 (234)	1/1 + 1/1 (226) (235)	3	2.9_6	91
4 Na(2)	—	1/1 (242)	—	—	1/1 (231)	1/1 (229)	1/1 (247)	4	3.8_5	96
4 Na(3)	—	1/1 (244)	—	—	1/1 (242)	1/1 (236)	1/1 (238)	4	3.9_7	100
4 Na(4)	1/1 + 1/1 (239) (240)	—	1/1 (241)	1/1 (242)	—	—	—	4	4.0_0	100
4 Na(5)	—	1/1 (234)	1/1 (231)	1/1 (233)	1/1 (222)	—	—	4	3.9_3	89
4 Na(6)	—	1/1 (238)	—	1/1 (245)	1/1 (240)	1/1 (232)	—	4	3.9_5	98
4 Na(7)	—	1/1 (252)	—	1/1 (288)	1/1 (234)	1/1 (234)	1/1 (241)	4 + 1	4.1_1	100
C.N.	6	6	5	5 + 1	6	6	6			
ECoN[c]	5.7_4	5.9_5	4.9_0	5.2_7	5.9_3	5.7_6	5.4_5			
MEFIR	141	143	139	142	139	136	139			

Note. The starting values of the ionic radii were determined basing on the ECoN concept: 140 (standard: $R(O^{2-})$) is subtracted from $\bar{d}$(Me—O).

[a] Distances and MEFIR in pm, SD: 0–2 pm.

[b] ECoN (Me/ΣO).

[c] ECoN (O/ΣMe).

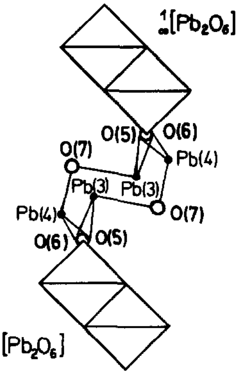


FIG. 30. Basic structural features of $Rb_2Pb_2^{2+}Pb_2^{4+}O_7$. Connection of the $^1_\infty[Pb_2O_6]$ chains by $[Pb^{II}O_3$ L.P.E.] tetrahedra.

(*138*) with isolated $[PbO_3]$-groups building a double-layer, like those of an oxoplumbate(IV) $A_4[PbO_4]$ (*39–42*) with isolated $[PbO_4]$-tetrahedra (see Table XLV). $KNa_7Pb_2O_7$ might be regarded as a derivative of $KNa_3[PbO_4]$ *and* $Na_4[PbO_3]$, both yet unknown.

XXIV. Disproportionation and Conproportionation with Oxostannates(II)

As early as 1931 first attempts were made to prepare, e.g., $BaSnO_2$ (*140*), still unknown today. For years all our attempts to synthesize, e.g., K_2SnO_2, starting with SnO

TABLE XLVI

Disproportionation with Oxostannates(II)

The "old story approach"	New approach	New routes
$2KO_{0.5} + 2Sn^{II}O \xrightarrow[600\text{–}700°C]{10d} K_2Sn^{IV}O_3 + Sn^0$	(1) $2KSn + \tfrac{3}{2}O_2 \xrightarrow[320°C]{6h} LT\text{—}K_2Sn_2^{II}O_3$ Isotypic with $K_2Pb_2O_3$	(1) $2Sn^0 + 2K_2HgO_2 \xrightarrow[550°C]{3d} HT\text{—}K_2Sn_2O_3 + 2Hg + K_2O$
The "next approach" $2KO_{0.48} + 2Sn^{II}O \xrightarrow[550°C]{10d} HT\text{—}K_2Sn_2^{II}O_3$	(2) $2KO_{0.48} + Sn^{IV}O_2 + Sn^0 \xrightarrow[500°C]{3d} HT\text{—}K_2Sn_2^{II}O_3$	(2) $Sn^0 + Sn^{IV}O_2 + 8NaO_{0.45} \xrightarrow[680°C]{2\text{–}66d} 2Na_4[Sn^{II}O_3]$
	(3) $KGe \xrightarrow[500°C]{O_2/4d} K_2Ge_2^{II}O_3$	(3) $2NaSn + 3Na_2O_2 \xrightarrow[550°C]{8d} 2Na_4[SnO_3]$
		(4) But: $4NaO_{0.48} + SnO \xrightarrow[700°C]{7d} Na_4[SnO_3]$

and K_2O, failed. Finally we believed that traces of K_2O_2, always present in K_2O prepared by oxidation of metallic K leads to the formation of K_2SnO_3. This K_2O_2 could act as a starter in the disproportionation $2K_2SnO_2 = K_2SnO_3 + K_2O + Sn$. Indeed, we always obtained metallic Sn in addition to K_2SnO_3.

In the first experiment starting with (underoxidized) $KO_{0.48}$ we immediately obtained $K_2Sn_2O_3$ (*116*) and other stannates (II) like Rb_2SnO_2 (*141*) by using the corresponding underoxidized AO_x ($x < 0.5$).

A more detailed investigation (*142*) then showed, that it is also the temperature and other factors, which play an important role. This is summarized in Table XLVI.

XXV. Oxoborates

Table XLVII shows the collection of new oxoborates we have prepared recently while hunting for the "true" orthoborates of the type $A_5[BO_4]$ (*150*). All our experiments to prepare the latter compounds are still without success. Since oxides like $NbBO_4$ (*151*) are known, and in borates which are "poor" in cations, B^{3+} quite easily adopts tetrahedral coordination it is not a simple matter to understand these observations.

Here we draw attention to the fact that all borates shown in Table XLVII have a common structural peculiarity. In all cases the CP of the "cations" Na^+, K^+ or Cs^+ are very distorted. We still do not know how to describe them in a manner that one can immediately understand what they are. Of course this is due to the fact that the $[BO_3]^{3-}$ group is unique in the case of oxo anions. There is no other corresponding group so small in size and so high in charge as this one. In combination with the unusual short distances d(O—O) within the group and its unmanageable size, a higher C.N. of Na^+, etc. can be realized only if some of the ligands belong to the same $[BO_3]$ group, thus leading to unusual short

TABLE XLVII

Monoborates of Alkali Metals

Ternary compounds	*a*	*b*	*c*	*β*	Reference
$Li_3[BO_3]$	326.5(1)	918.0(3)	831.6(3)	101.05(2)°	(*143*)
$Na_3[BO_3]$	568.7(2)	753.0(1)	999.3(5)	127.15(4)°	(*144*)
	Both $P2_1/c$, completely different in structure!				
Quaternary compounds					
$NaLi_2[BO_3]$	950.7(4)	1203.7(3)	1172.0(4)	155.91(6)°	(*150*)
$Na_2Li[BO_3]$	1402.2(3)	500.9(1)	874.5(2)	98.84(3)°	
$Na_4Li_5[BO_3]_2$	1238.8(5)	729.6(3)	973.8(3)	107.29(4)°	(*148*)
$KLi_2[BO_3]$	797.1(4)	643.2(3)	645.7(3)	90°	(*145*)
$K_2Li[BO_3]$	876.1(3)	608.1(2)	735.4(3)	102.57(5)°	(*146*)
$KNa_2[BO_3]$	603.9(2)	560.2(3)	556.8(2)	90°	(*147*)
$RbLi_2[BO_3]$	811.3(3)	645.7(2)	655.3(2)	90°	(*150*)
$CsLi_5[BO_3]_2$	1179.5(4)	943.3(3)	809.6(2)	132.76°	(*149*)

TABLE XLVIII

CATIONIC ENVIRONMENT OF THE $[BO_3]$ GROUPS

	Angular		Terminal		
	Small	Large	Small	Large	Σ
$Li_3[BO_3]$	1		10		11
$NaLi_2[BO_3]$	1	1	7	4	13
	1	2	6	2	9
$Na_2Li[BO_3]$		4	4	4	12
$Na_3[BO_3]$	2		10		12
$Na_4Li_5[BO_3]_3$	1	3	5	4	13
	1	2	6	4	13
$KLi_2[BO_3]$	2	2	4	5	13
$KNa_2[BO_3]$	2	2	6	2	12
$K_2Li[BO_3]$	1	3	2	8	14
$CsLi_5[BO_3]_2$	1	2	8	2	13

distances d(O—O) within the CP of A^+. But if we are unable to master this problem how could we hope to deal with crystal chemistry at all?

In addition, even the most simple facts of this case are still unexplainable. In Table XLVIII we have collected data showing how each of the $[BO_3]$ groups in the different cases is surrounded by the cations A^+. As far as we see there is no simple explanation available for the details of the motifs of these surroundings.

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