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Crystal Structure of a New Oxyfluoride: $Tl_2Zr_3OF_{12}$

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A new family of oxyfluorides with formula $A_2B_3OF_{12}$ (A = Rb, Tl, NH_4; B = Zr, Hf) has been synthetized. The crystal structure of $Tl_2Zr_3OF_{12}$ has been determined from single crystal X-ray diffraction data collected with a Nonius CAD-4 automatic diffractometer. $Tl_2Zr_3OF_{12}$ crystallizes in the rhombohedral system, space group $R\bar{3}m$ (No. 166), with hexagonal lattice parameters $a = 7.703(1)$ Å and $c = 30.017(2)$ Å, $Z = 6$. The structure was solved by conventional Patterson and Fourier methods and refined by full matrix least-squares techniques to a conventional R of 0.046 ($R_\omega = 0.063$). The structure analysis, using different methods for evaluating the valence-bond distributions according to various modifications of the Pauling electroneutrality principle, has been carried out and has shown an ordered oxygen–fluorine distribution within the anionic sublattice. The structure consists of double layers of edge-shared and corner-shared distorted square antiprisms ZrX_8 (X = F,O). The double layers running perpendicularly to the c hexagonal lattice axis have a stacking sequence ABC, ABC, . . . , and are bonded together by the Tl^+ ions. Comparison with other structural types, namely KY_3F_{10}, β-KYb_3F_{10}, $Na_7Zr_6F_{31}$, and fluorite, are discussed as far as the arrangements of cation centered square antiprisms are concerned.

Introduction

The increasing need of efficient materials suitable for use in electrochemical devices leads the solid state chemist to investigate new binary or ternary systems in order to discover compounds having high performance. In this connection fluorides are of special interest for use as separators because they are electronic insulators and exhibit pure ionic conductivity.

Some time ago we reported results of our investigations on the TlF–ZrF_4 system (*1*) as well as details of parts of it (*2, 3*). Since, we have extended this work to the study of the ternary TlF–ZrF_4–ZrO_2 system because of the potential interest presented by some oxyfluorides as solid electrolyte due to their thermodynamic and chemical stabilities being better than those of fluorides and due to their ability to give ceramics with high compactnesses. This investigation has allowed us to find a well-characterized compound with formula $Tl_2Zr_3OF_{12}$ and to determine its crystal structure. The relationship between this structure and that of the fluorite, as well as the role played by oxygen in stabilizing this structural type, is discussed.

Experimental

Crystals of $Tl_2Zr_3OF_{12}$ were grown by slowly cooling a melt with a $2TlF + 2.5ZrF_4 + 0.5ZrO_2$ composition in a platinum tube sealed under a dry argon atmosphere.

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The ZrO_2 was obtained from Merck (selectipur) and both TlF and ZrF_4 were prepared in the laboratory according to the methods described previously (*3*).

The samples were heated for 8 hr at 550°C and then cooled to room temperature at the rate of 3°C/hr.

Clear colorless platelike crystals were obtained and identified as $Tl_2Zr_3OF_{12}$ crystals by comparison of the X-ray powder diffraction pattern of ground single crystals to that from a bulk preparation of $Tl_2Zr_3OF_{12}$ previously established in the laboratory and given in Table I.

Single Crystal Diffraction Data

A preliminary study using Weissenberg and precession methods indicated a trigonal Laue symmetry $\bar{3}m$. The systematic extinctions hkl: $-h + k + l \neq 3n$ are consistent with space groups $R\bar{3}m$, $R3m$, or $R32$.

A nonlinear optical test based on second-harmonic generation experiments has been carried out on a polycrystalline sample.[1] As no second-order effect has been observed it was not possible to deduce any indication concerning the absence or presence of a center of inversion. So, in absence of contrary information the $R\bar{3}m$ group was retained for the analysis and this choice was subsequently carroborated by the structure refinement.

The hexagonal unit cell parameters were determined accurately using an automatic four-circle Nonius CAD-4 diffractometer by centering on 21 reflections and refining by least-square techniques.

Crystal data. $Tl_2Zr_3OF_{12}$, $M = 926.38$; $a = 7.703(1)$ Å and $c = 30.017(2)$ Å; $D_m = 5.94$ g/cm^3, $D_c = 5.98$ g/cm^3 for $Z = 6$.

Intensity measurements. Intensity measurements were made on a crystal with approximate dimensions 0.082 × 0.17 × 0.22 mm.

TABLE I

X-RAY POWDER DATA FOR $Tl_2Zr_3OF_{12}$

$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	h	k	l	I/I_0
6.53	6.51	1	0	1	5
6.12	6.10	0	1	2	6
5.03	5.00	0	0	6	12
4.48	4.46	0	1	5	5
3.87	3.85	1	1	0	22
3.62	3.61	1	0	7	74
3.33	3.34	0	0	9	89
3.29	3.31	0	2	1	100
	3.27	0	1	8	
3.07	3.05	1	1	6	62
2.920	2.916	2	0	5	9
2.740	2.737	1	0	10	8
2.637	2.633	0	2	7	4
2.529	2.526	0	1	11	5
2.499	2.501	0	0	12	11
	2.493	2	0	8	
2.233	2.231	0	2	10	11
2.182	2.182	1	0	13	23
2.115	2.112	2	0	11	22
2.098	2.098	1	1	12	31
2.043	2.041	0	1	14	47
2.004	2.001	0	0	15	25
1.928	1.926	2	2	0	53
1.853	1.852	1	2	11	9
1.807	1.804	2	0	14	19
1.701	1.699	1	3	7	12
1.668	1.668	2	2	9	21
1.663	1.665	4	0	1	31
1.635	1.633	1	2	14	12
1.573	1.575	1	3	10	4

Data were collected using an $\omega - 2\theta$ scan technique and Mo$K\alpha$ radiation monochromated with a flat graphite monochromator crystal ($\lambda = 0.71069$ Å). Three reflections measured at 120-min intervals showed no systematic variation in intensity (the relative standard deviation is 0.02). The orientation was checked after every 200 reflections.

Intensities of 1225 reflections were registered in the FLAT (see Ref. (*3*)) mode over the range $1 < \theta < 40$ and reduced to 908 with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied, followed by an absorption correction ($\mu = 325.29$ cm^{-1})

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[1] The authors thank Mr. Durand of the University of Montpellier for performing this test.

made with the program AGNOST using the De Meulaner and Tompa's analytical method (*4*) (minimum absorption correction 0.014, maximum 0.133).

Structure Solution and Refinement

The heavy atom positions were deduced from the Patterson function[2] and the calculation of structure factors resulted in $R = \Sigma|F_o| - |F_c|/\Sigma|F_o| = 0.177$.

Three subsequent cycles of refinement involving the cationic positions and isotropic thermal parameters led to an R value of 0.129.

With this data a Fourier synthesis revealed the five independent anionic positions. Subsequent full-matrix least squares refinement using isotropic thermal parameters gave an $R = 0.078$. The scattering factors for Tl^+, Zr^{4+}, F^-, and O^{2-} ions were taken from the *International Tables for X-Ray Crystallography* (*5*) as were the anomalous dispersion terms for Tl and Zr for Mo$K\alpha$ radiation. Final refinement in which only the cations were assigned anisotropic thermal parameters led to $R = 0.046$ ($\omega R = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2]^{1/2} = 0.067$). The final parameters with their estimated standard deviations are listed in Table II. A list of the observed and calculated structure factors can be requested from the authors.

TABLE II

FINAL VALUES OF ATOMIC PARAMETERS AND THERMAL PARAMETERS ($\times 10^4$)[a,b] FOR $Tl_2Zr_3OF_{12}$

Atom	Position	x	y	z	$B_{eq.}$ (Å^2)
Tl(1)	3*a*	0	0	0	1.3(.1)
Tl(2)	3*b*	0	0	5000	1.1(.1)
Tl(3)	6*c*	0	0	1392(1)	2.0(.1)
Zr	18*h*	5155(1)	−5155	601(0)	0.3(.1)
F(1)	18*f*	3521(11)	0	0	0.7(.1)
F(2)	18*h*	1424(9)	−1424	2078(4)	1.4(.2)
F(3)	18*h*	1638(9)	−1638	9263(3)	0.9(.1)
F(4)	18*h*	2236(7)	−2236	713(3)	0.7(.1)
O	6*c*	0	0	2877(7)	0.4(.2)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl(1)	33(2)	β_{11}	8(0)	16(0)	0	0
Tl(2)	64(2)	β_{11}	3(0)	32(0)	0	0
Tl(3)	128(2)	β_{11}	4(0)	64(0)	0	0
Zr	12(1)	β_{11}	1(0)	8(2)	0.1(.2)	$-\beta_{13}$

[a] Standard deviations are given in parentheses.

[b] The expression for the thermal factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Assignment of the Oxygen Position and Discussion

Generally X-ray crystal structure determination does not allow to distinguish between fluorine and oxygen atoms incorporated in inorganic ionic crystal structures because both O^{2-} and F^- anions possess very close scattering factors as well as similar ionic radius. Moreover as they have also close electronegativities they can occupy the same kind of sites with some randomness and it is always difficult to differentiate these two anions. A recent attempt to distinguish them has been made using NMR techniques and second moments calculation (*6*). However, this method give satisfactory results only when the cation–anion distances range over a relatively large extent so that there is enough difference between them as they intervene (at the reciprocal 6th power) in the calculations.

The aim of this paper is to draw attention to the fact that Pauling's principle of local neutralization of charges (*7*) can solve the problem at hand. Thus the analysis of the local balance of valences makes it possible to assign or more exactly to confirm the oxygen positions. To deal with this problem we used three methods which gave thoroughly convergent results: Zachariasen's method (*8*), Pyatenko's method (*9*), and Donnay and Allmann's method (*10*).

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[2] The authors acknowledge the technical assistance rendered by M. Gasparin of the P. and M. Curie University (Laboratory of Mineralogy and Crystallography, 4, place Jussieu, 75230 Paris) in performing the computation of this function.

TABLE III

VALENCE BALANCE FOR $Tl_2Zr_3OF_{12}$

		0.5F(2) (18*h*)	0.1666O (6*c*)	0.5F(1) (18*f*)	0.5F(4) (18*h*)	0.5F(3) (18*h*)	$\Sigma_i s_{ij}$
0.5Zr	(18*h*)	0.355	0.122	0.229	0.225	0.205	2.039
0.0833*Tl*(1)	(3*a*)			0.018	0.0016	0.007	0.080
0.0833*Tl*(2)	(3*b*)	0.013			0.005		0.054
0.1666T1(3)	(6*c*)	0.029 0.002			0.004	0.020	0.086
$\Sigma_j s_{ij}$		0.444	0.366	0.512	0.476	0.461	2.26/2.26
v_j (calc.)		0.89	2.20	1.02	0.95	0.92	
v_j (th.)		1	2	1	1	1	

(*a*) *Zachariasen's Method*

This method is an empirical bond length–bond strength method of interpretation and has been applied to bond lengths observed in each of the cation coordination polyhedra. This approach could be used successfully since bond lengths presented in Table VI are known with reasonable accuracy (σ = 0.02 Å or less). Table III shows the results of our analysis by this method. The values reported in this table have been obtained using the general relationship

$$D(s) = D(1) - B \ln s \qquad (1)$$

given by Zachariasen (*8*) where $D(1)$ values of 1.83, 1.962, and 2.10 Å for Zr–F, Zr–O, and Tl–F bond lengths have been used, respectively, as well as B values of 0.4 for both Zr–F and Tl–F bonds and 0.326 for the Zr–O bond. The value of 1.962 for the Zr–O bond length is that given by Table 1 in Ref. (*8*). The value of 1.83 Å for the Zr–F bond length $D(1)$ has been calculated from data of several crystal structures determinated with sufficient accuracy (*11, 12, 3*) using the formal value for s ($s = Z/N$ where Z is the cation charge and N the coordination number) and the value of 0.4 for the B coefficient of Eq. (1) as suggested by Zachariasen. The value of 2.10 Å for the Tl–F bond length $D(1)$ has been obtained by a similar calculation with data from Refs. (*3*) and (*13*).

(*b*) *Pyatenko's Method*

This method is based upon the assumption that in each coordination polyhedron the magnitudes of the valence forces of the cation v_i transmitted directly to its surrounding i anions are inversely proportional to the nth power of the cation–anion distance r:

$$v_i = \frac{k_j}{r_i^n}.$$

For each specific polyhedron in a specific structure, the k_j value is constant and is determined from the equation $\Sigma_i k_j / r_i^n = v_c$ where v_c is the valence of the cation; thus,

$$k_j = v_c / \sum_i 1/r_i^n.$$

The obtained results are presented in Table IV.

For the zirconium polyhedron the n value was taken in Table I of Ref. (*9*) while for T1 polyhedra the n value was estimated to be

TABLE IV

LOCAL BALANCE OF VALENCES IN THE STRUCTURE OF $Tl_2Zr_3OF_{12}$

Atoms	Wyckoff position	Coordinance	$v_{calc.}$	$v_{th.}$
F(2)	19*h*	1Zr + 1Tl(3) + 1Tl(2)	0.98	1
O	6*c*	3Zr	1.66	2
F(1)	18*f*	2Zr + 1Tl(1)	1.07	1
F(4)	18*h*	2Zr + 1Tl(2)	1.0	1
F(3)	18*h*	2Zr + 1Tl(3) + 1Tl(1)	1.07	1

TABLE V

ESTIMATED BOND VALENCES IN $Tl_2Zr_3OF_{12}$

Atoms	Wyckoff position	Coordinance	$v_{calc.}$	$v_{th.}$
F(2)	18*h*	1Zr + 1Tl(3) + 1Tl(2)	1.04	1
O	6*c*	3Zr	1.71	2
F(1)	18*f*	2Zr + 1Tl(1)	1.08	1
F(4)	18*h*	2Zr + 1Tl(2)	0.99	1
F(3)	18*h*	2Zr + 1Tl(3) + 1Tl(1)	1.06	1

equal to 6 from data relating to Tl–F bond lengths in $TlUF_5$ (*13*) and $TlZrF_5$ (*3*) structures as well as from electronegativity considerations.

(*c*) *Donnay and Allmann's Method*

This method is based on two equations:

$$v = v_i \left(\frac{\bar{L}}{L}\right)^p \qquad \text{for } L \le \bar{L}$$

$$\text{with } p = \frac{\bar{L}}{L_{\max} - \bar{L}}$$

and

$$v = v_i \left(\frac{L_{\max} - L}{L_{\max} - \bar{L}}\right) \qquad \text{for } \bar{L} \le L_{\max}$$

where $\bar{L}$ is the mean bond length of the cation polyhedron found in the structure under consideration. $L_{\max}$ is the largest cation–anion distance that can be considered a bond and v_i the ideal bond valence.

The $L_{\max}$ value of 2.58 Å for the Zr–F bond used in this calculation has been obtained by subtracting 0.07 Å from the Zr–O bond length value given in Table 2 of Ref. (*10*) as has been suggested by the authors in this paper. As far as the Tl–F bonds are concerned, only Tl–F bond lengths shorter than 3.43 Å have been taken into account in this calculation although distances as large as 3.89 Å belong the thallium coordination polyhedra. This value of 3.43 Å has been obtained by subtracting 0.07 Å also from the Tl–O maximum bond length given in Table 2 of Ref. (*10*). The electrostatic valences calculated under these conditions are listed in Table V.

Discussion

Donnay and Allmann's method as well as Pyatenko's method lead to values of 1.66 and 1.71, respectively, for the oxygen electrostatic valence (theoritical value: 2) and to values not significantly different of 1 for fluorine (theoritical value: 1). The obtained values for *F*(1), *F*(4) and *F*(3) are perfectly consistent while a small discrepancy has been registered for *F*(2).

From these results the presence of OH at the 6*c* site cannot be ruled out but this assumption is inconsistent with the charge equilibrium if the cationic ratio Tl/Zr is considered to be constant and equal to $\frac{2}{3}$ and the formal charges of Tl and Zr equal to +1 and +4, respectively.

However, as the baddeleyite crystal structure determination (*14*) has pointed out that the shortening of some of the Zr–O distances in the seven-pointed coordination structure of this dioxide could be attributed to a deficiency of positive valence forces converging on the respective oxygen atom, the possibility for the Zr atoms exhibiting some defects in their positive charges cannot be ruled out. Furthermore the general statement that the decrease in the cation–anion distances must be related to defects in the local compensation of valences has been reported and discussed by Baur (*15*).

As far as Zachariasen's method is concerned the obtained results relating to the anionic electrostatic valences, mentioned in Table III, corroborate our assignment of the oxygen position as well as the $Tl_2Zr_3OF_{12}$ formula proposed from our crystallographic results. The calculated anionic electrostatic valence v_j was obtained multiplying $\Sigma_j s_{ij}$ by the inverse of the atom multiplicity given in the first line of the table.

In view of results of the analysis by these three methods it seems that this structure should be ordered as far as the anionic sublattice is concerned and hence

TABLE VI

SELECTED BOND LENGTHS FOR $Tl_2Zr_3OF_{12}$ (Å)

Tl(1)–F(1)	(× 6)	2.713(9)	Zr–F(2)		1.967(12)
Tl(1)–F(3)	(× 6)	3.111(10)	Zr–O		2.063(5)
Tl(1)–F(3)	(× 6)	3.671(8)	Zr–F(1)	(× 2)	2.143(5)
Tl(2)–F(2)	(× 6)	2.832(12)	Zr–F(4)	(× 2)	2.147(2)
Tl(2)–F(4)	(× 6)	3.217(4)	Zr–F(3)	(× 2)	2.188(6)
Tl(3)–F(2)	(× 3)	2.802(12)			
Tl(3)–F(3)	(× 3)	2.941(10)			
Tl(3)–F(4)	(× 3)	3.614(8)			
T1(3)–F(2)	(× 6)	3.888(2)			
F(1)–F(1)		2.279(17)	F(2)–F(3)		2.615(11)
F(1)–F(3)		2.600(8)	F(2)–F(4)		2.749(11)
F(1)–F(4)		2.611(2)	F(3)–F(4)		2.676(7)
F(1)–F(1)		2.713(9)	F(4)–F(4)		2.537(16)
F(1)–O		2.849(11)			
O–F(3)		2.414(13)			
O–F(2)		3.059(20)			
Tl(1)–Tl(3)		4.179(3)	Tl(1)–Zr		4.258(1)
Zr–Zr		3.493(2)	Tl(2)–Zr		4.020(1)
Zr–Zr		3.629(1)	Tl(3)–Zr		4.500(3)

we will give a description of it in the following section in considering it as such. This result has been confirmed by a site potential calculation.[3]

Description of the Structure and Discussion

The Zr^{4+} ion is coordinated by seven fluorine atoms and an oxygen atom in a polyhedron which may be regarded as a distorted square antiprism according to the Lippard and Russ definition of an eight coordinate polyhedron (*16*). The Zr–X (X = F,0) distances ranging from 1.97 to 2.19 Å are presented in Table VI. Three square antiprisms share, around a common corner O, three edges O–F(3) to form a ($Zr_3F_{18}O$) entity (Fig. 1a) while three others by sharing F(4) corners form a ($Zr_3F_{18}O_3$) entity (Fig. 1b). Both ($Zr_3F_{18}O$) and ($Zr_3F_{18}O_3$) entities share three edges involving the shortest F(1)–F(1) distances to generate a ($Zr_6F_{30}O_4$) polyanion enclosing an empty cavity and which may be regarded as the basic structural unit. Each (Zr_6X_{34}) polyanion is linked to six others by the sharing of external corners and edges of square antiprisms namely the F(4) corner and the O–F(3) edges to form a double layer of (ZrX_8) polyhedra (Fig. 2).

Such a packing of the polyanions delimits channels where the Tl(1) ions lie and are surrounded by $18F^-$. The complete structure can be described as a stacking of such layers perpendicularly to the c axis with the sequence ABC, ABC, ...

These layers are bound together by the Tl(2) and Tl(3) ions which are coordinated by 12 and 15 F^-, respectively.

It is interesting to compare the stacking of Archimede's square antiprisms in this structure with those occuring in various ordered phases related to the fluorite structure by anion excess and to the β-KYb_3F_{10} structural type (*17*). As has been reported by Frit and Laval (*18*), these ordered phases related to the fluorite structure can fall into two large families corresponding to two different ways to associate MX_8 antiprisms in clusters. In this respect only the former, including $M$$Ln_3F_{10}$ compounds (*19, 20*), $Na_7Zr_6F_{31}$ (*11*), and tveitite $Ca_{13}Y_6(O,F)_{44-\delta}$ (*21*), are of interest. The cluster is made up of six antiprisms associated in a finite group and delimiting a cuboctahedral cavity. Moreover, depending on whether the octahedral cavity is empty or, on the contrary, occupied by an additional anion, the anionic excess relating to this cluster is of four or five anions, in comparison with the fluorite, leading to the M_6X_{36} or M_6X_{37} formula.

Thus in the fluorite structure the Ca_6F_{32} cluster consists of an empty anionic cube surrounded by six cation-centered anionic cubes. In both $Na_7Zr_6F_{31}$ and tveitite structures the M_6X_{37} cluster consists of an octahedral arrangement of cation-centered square antiprisms sharing corners to enclosed a filled cuboctahedron of anions.

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[3] The authors are grateful to Dr. J. Pannetier, ILL Grenoble, for carrying out this computation.

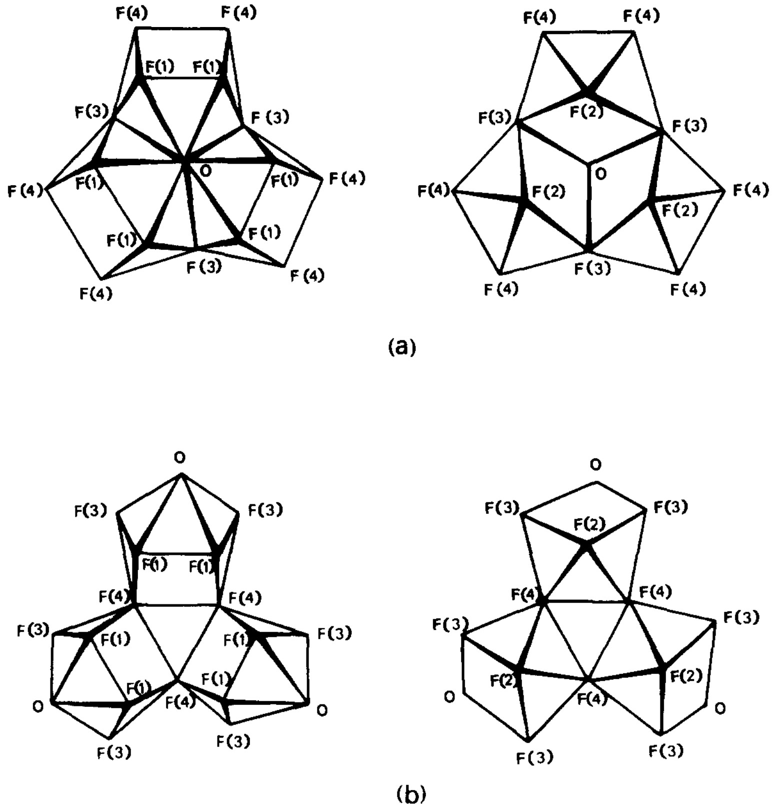

FIG. 1. (a) $(Zr_3F_{18}O)^{8-}$ entity; (b) $(Zr_3F_{18}O_3)^{12-}$ entity. For both views of the entities (a) and (b) along the threefold axis, the left-hand side and the right-hand side represent bottom and top views, respectively, or vice versa.

This unit is derived very simply from the fluorite element described above by a 45° rotation of the inner faces of each cubes as shown by Bevan *et al.* (*21*). In the KY_3F_{10}-type phases (*19*) a M_6X_{36} cluster occurs which derives from the fluorite element by a 45° rotation of the inner faces of the anionic cubes. Let us note that these units are connected in such a way as to generate M_6X_{32} groups (*21*).

The β-KYb_3F_{10}-type phases (*17*) are characterized by the occurrence of M_6X_{32} clusters which derives from the fluorite element by a 45° rotation of the outer faces of the anion cubes. The M_6X_{34} cluster observed in the $Tl_2Zr_3OF_{12}$ structure is previously unknown and lies halfway between the M_6X_{32} (encountered in β–KYb_3F_{10}) and $M_6X_{36(\text{or } 37)}$ units in the sense that it consists of an arrangement of three antiprisms sharing, around a common corner, three edges as in M_6X_{32} and three antiprisms sharing corners only as in $M_6X_{36(\text{or } 37)}$. These two half-entities are connected together by sharing of three edges.

In addition, the role played by oxygen in obtaining such a packing of antiprisms surrounding a tetravalent cation such as Zr^{4+} must be emphasized. Indeed, because of Pauling's electrostatic valence rule it is necessary that the corner shared by three antiprisms should be occupied by an oxygen atom and points to a long-range order in the anion sublattice.

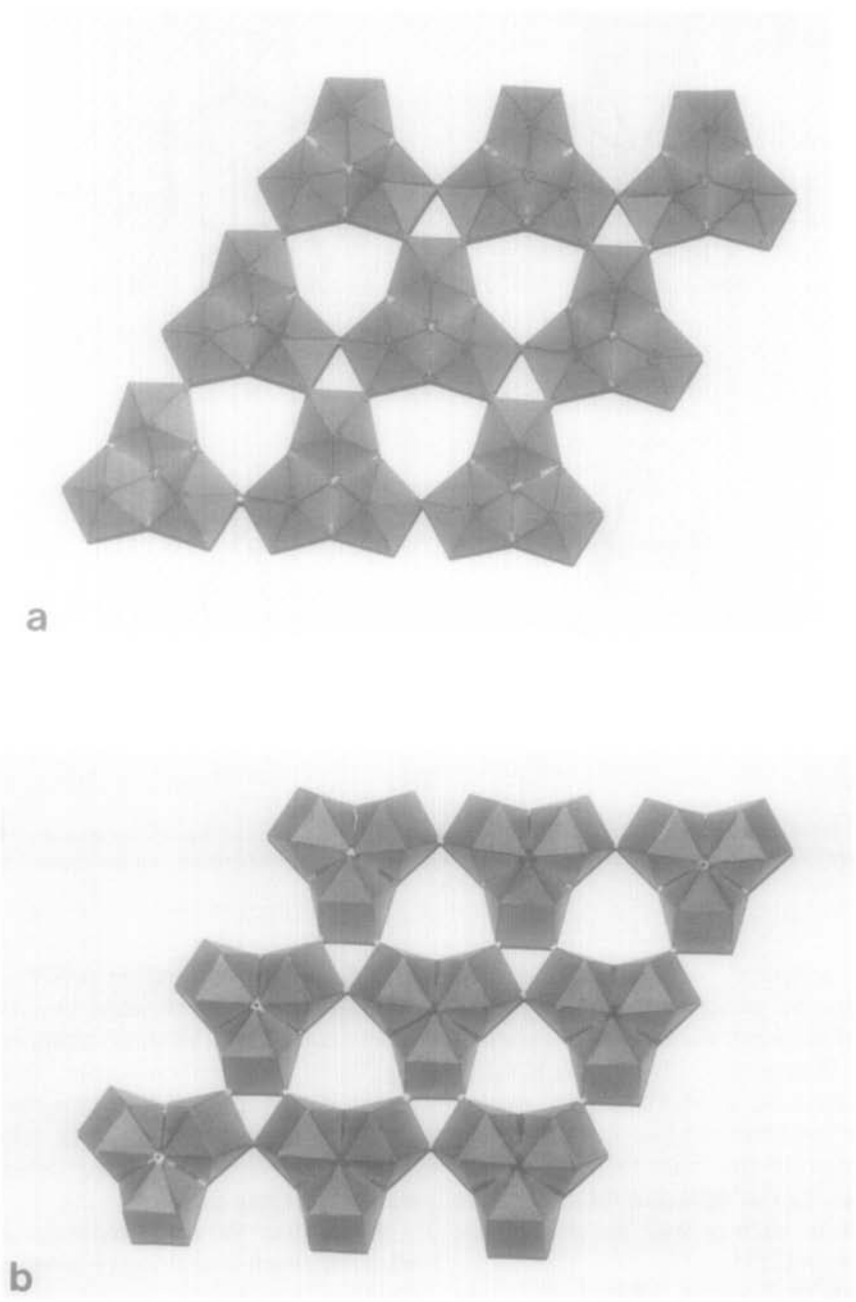

FIG. 2. Polyhedral representation of layers of ZrX_8 antiprisms in $Tl_2Zr_3OF_{12}$ as viewed along the *c* hexagonal lattice axis. (a) Top view of the single layer, (b) bottom view of the single layer, (c) the double layer.

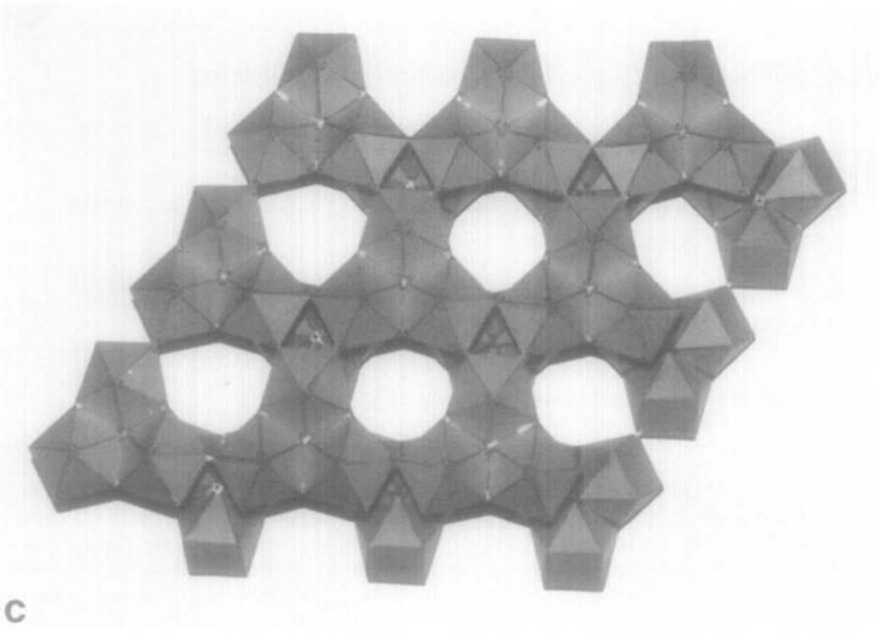

FIG. 2—*Continued.*

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