Simplified Description of Complex Structures from Stackings of UGP

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A simplified description of complex structures is proposed. The method consists in defining a geometrical unit of polyhedra, called UGP. Then, a three-dimensional network is built up from simple stackings of these UGP. Cationic sites and additional anionic sites are generated from the stacking of UGP. An explicit formulation "counterions[network]additional ions" summarizes the structure description. This method is applied to numerous structures that involve square antiprisms and can be used for other polyhedra. © 1997 Academic Press

INTRODUCTION

In our preceding publication (1), the fluoride $(H_3O)Yb_3F_{10}, H_2O$ was described utilizing a diamond-type stacking of octahedral units of antiprisms, called $UOA_{[8]}$, in which the structural description was highly simplified.

A bibliographic search concerning structures involving square antiprisms yielded many examples of complex descriptions based on the connections between polyhedra. By studying these structures, it was always possible to find a simplifying way of description, provided that the basic unit was well defined. The general principle is to define a suitable *geometrical unit of polyhedra*, called **UGP**, which is the basis of the simple stacking. Then the resulting three-dimensional network of **UGP**, considered as a stacking of spheres, generates sites of variable coordination in which counterions are located. Moreover, anionic sites, located at the center of the **UGP** or due to the particular geometry of the vacant space between the **UGP**, may be filled by supplementary ions. This method allows a summarization of a structural description by the explicit formulation "**counterions[network]additional ions**," with the appropriate formula unit **Z**.

In this paper, we report the simplifying descriptions of several structures mainly based on square antiprisms. They are described from **UGP** whose names are **UOA$_{[8]}$** and

UOA$_{[12]}$ (**UOA** means octahedral unit of antiprisms and the number between square brackets refers to the vacant anionic cavity located at the center of the UGP; 8 refers to a cube, 12 refers to a cuboctahedron). For the sake of clarity, structures have been classified as a function of their type of stacking: compact, semicompact, and noncompact.

1. STRUCTURES WITH A COMPACT STACKING OF UOA$_{[8]}$

1.1. ABA … Type (Hexagonal Close Packing)

The low-temperature form of β-KYb$_3$F$_{10}$ (2) is hexagonal (S.G.: $P6_3mc$, $a = 8.067(2)$ Å, $c = 13.203(4)$ Å, $Z = 4$) and is based on square antiprisms connected by vertices and edges. The authors noticed the existence of $[Yb_6F_{32}]^{14-}$ clusters, but their description was based on layers involving only three antiprisms (half of an $UOA_{[8]}$). In fact, the c/a ratio (1.637) is very close to the ideal value ($2\sqrt{2/3} = 1.633$) for a hexagonal close packing. As can be seen in Figs. 1a and 1b, this compound exhibits compact layers of $UOA_{[8]}$ superimposed along c, according to an ABA … stacking. Each $UOA_{[8]}$ has 12 neighboring $UOA_{[8]}$ ($3 + 6 + 3$ along c) linked by vertices. Two vertices are common to two $UOA_{[8]}$. Thus, the formulation of the three-dimensional network is Yb_6F_{20} ($Yb_6F_8F_{24/2}$), with **Z = 2**, and this phase is actually a hexagonal close packing (h.c.p.) of $UOA_{[8]}$. The A and B layers are presented in Figs. 2a and 2b, with an equivalent drawing from spheres. The calculated radius ($R = a_H/2$) for an $UOA_{[8]}$ in 12 coordination is equal to 4.04 Å. The h.c.p. network generates four sites of four-fold coordination and two sites of six-fold coordination. Half of the first sites are occupied by the $K_{(2)}^+$ ions, whose anionic coordination is $(4 + 12)$ F$^-$ (tetrahedral close coordination + cage). The second sites are not occupied, but the $K_{(1)}^+$ ions are situated near them with an anionic coordination of $(3 + 12)$ F$^-$ (truncated tetrahedral close coordination + cage). In summary, β-KYb$_3$F$_{10}$ is an h.c.p. of $UOA_{[8]}$, with K$^+$ ions situated in cavities of the network. Its formulation is **K$_2$[Yb$_6$F$_{20}$]**, with **Z = 2**.

Another example of this type stacking is given by $Zr_3F_8O_2$ (3), for which the c/a ratio is equal to 1.628
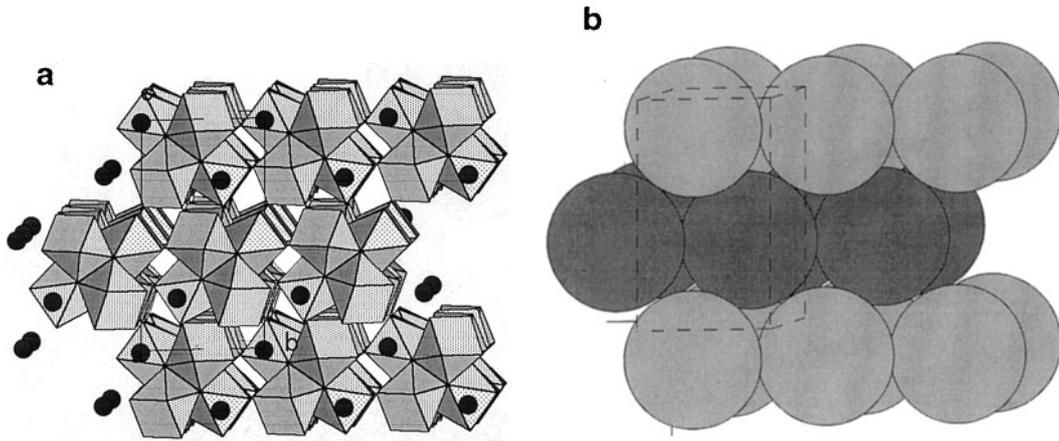
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FIG. 1. Perspective view of the ABA ... layers in β-KYb$_3$F$_{10}$ (a) from UOA$_{[8]}$ and (b) from spheres.

(S.G.: $P6_3mc$, $a = 7.771(5)$ Å, $c = 12.49(1)$ Å, $Z = 4$). This compound is based on ZrF$_6$O$_2$ square antiprisms. According to our method of description, these antiprisms share edges in order to form Zr$_6$(F$_4$O$_4$)F$_{24}$ UOA$_{[8]}$ linked only by fluorinated vertices. This leads to a neutral three-dimensional network: Zr$_6$(F$_4$O$_4$)F$_{24/2}$ = [Zr$_6$(F$_4$O$_4$)F$_{12}$]^0. Tetrahedral and octahedral sites of the h.c.p. of UOA$_{[8]}$ are free. The formulation is thus [**Zr$_6$F$_{16}$O$_4$**], with **$Z = 2$**.
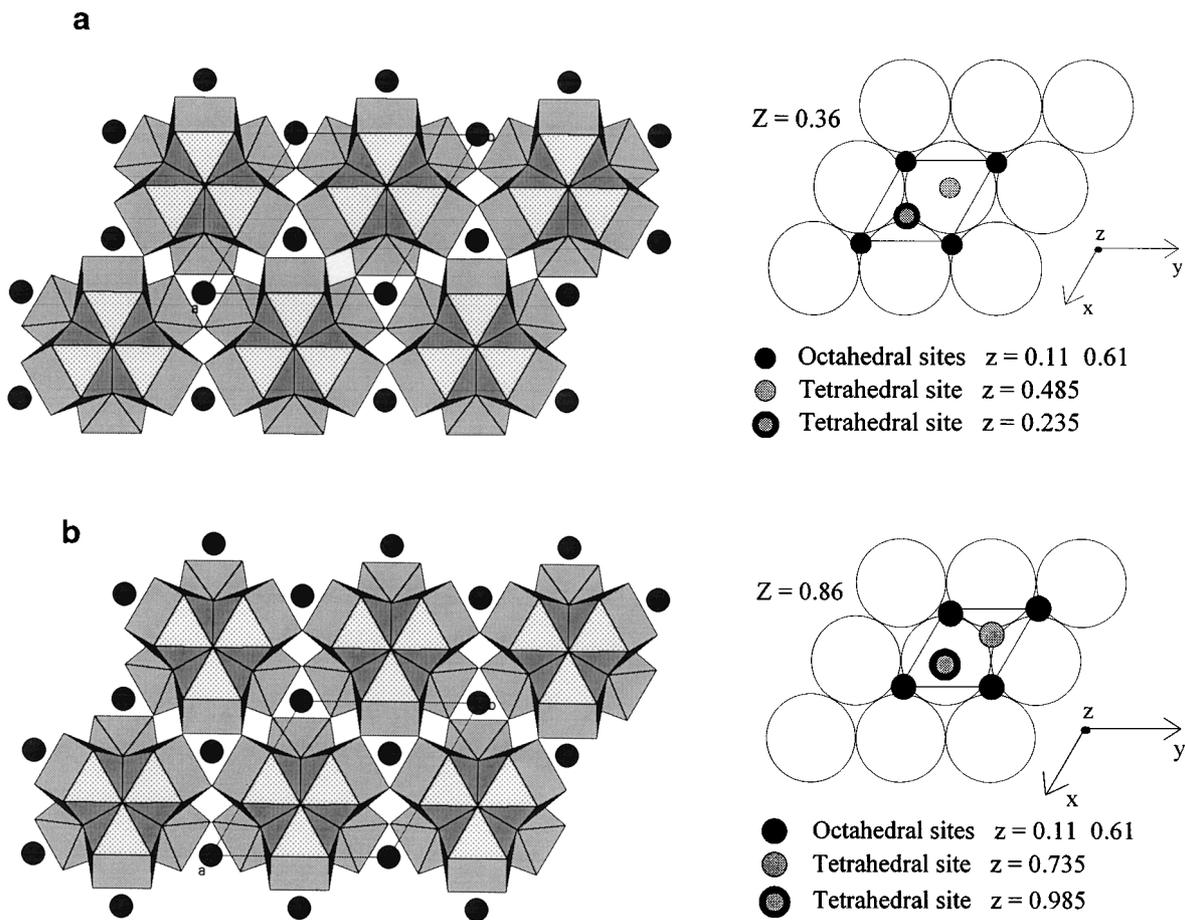

FIG. 2. (Left) Layers of β-KYb$_3$F$_{10}$ viewed along [001]. (a) Layer A centered on $z = 0.36$ ($0.11 < z < 0.61$) (K_1: 0 0 0.49, K_2: $\frac{2}{3}$ $\frac{1}{3}$ 0.24). (b) Layer B centered on $z = 0.86$ ($0.61 < z < 1.11$) (K_1: 0 0 0.99, K_2: $\frac{1}{3}$ $\frac{2}{3}$ 0.74). (Right) The same layers from spheres (the positions of vacant sites are given).

1.2. ABC ... Type (Cubic Close Packing)

Starting from the radius of an $UOA_{[8]}$ in the h.c.p. of β-KYb_3F_{10} ($R = 4.04$ Å), one can expect that the cell parameter of a cubic close packing (c.c.p.) of $UOA_{[8]}$ should be $a_c = 2R\sqrt{2} = 11.41$ Å. The cell parameter of the high-temperature form γ-KYb_3F_{10} (4) (S.G.: $Fm3m$, $a = 11.431$ Å, $Z = 8$) is close to this value. We have therefore reconsidered the description of this structure: this cubic phase is effectively based on $UOA_{[8]}$, centered on the $4a$ (0 0 0) position. As can be seen in Figs. 3a and 3b, this structure corresponds to a compact stacking of $UOA_{[8]}$ linked by vertices. Each $UOA_{[8]}$ is connected to 12 neighboring $UOA_{[8]}$. The formulation of the three-dimensional network is again Yb_6F_{20}, with $Z = 4$. Thus, 8 four-fold coordination sites and 4 six-fold coordination sites are present. The K^+ ions ($8c$: $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$) occupy the tetrahedral sites. Their anionic coordination is also tetrahedral (4 F^- at 2.57 Å, plus 12 F^- at 3.16 Å). Octahedral sites are free. The formulation of the structure is then $\mathbf{K_2[Yb_6F_{20}]}$, with $\mathbf{Z = 4}$. One can also consider this structure like an Li_2S anti-fluorite type for which $[Yb_6F_{20}]^{2-}$ stands for S^{2-} and K^+ stands for Li^+.

It is noticeable that the six-fold coordination sites correspond to the center of an empty cuboctahedral cavity built up from six antiprisms connected by vertices. Therefore, this cuboctahedron is the center of another octahedral unit of antiprisms, called $\mathbf{UOA_{[12]}}$, whose formulation is M_6X_{36}. Two views of an $UOA_{[12]}$ are given in Figs. 4a and 4b. The structure of γ-KYb_3F_{10} can then be described from $UOA_{[12]}$. Indeed, each vertex of an $UOA_{[12]}$ is common to three neighboring $UOA_{[12]}$. The formulation of the Yb_6F_{20}

three-dimensional network can be retrieved by the following relation: $Yb_6F_{36} \rightarrow Yb_6F_{12}F'_{24/3} \equiv Yb_6F_{20}$. Thus, a c.c.p. of edge sharing $UOA_{[12]}$ is observed by a $\frac{1}{2}$ 0 0 translation from the c.c.p. of vertex sharing $UOA_{[8]}$. The tetrahedral sites generated by the c.c.p. of $UOA_{[12]}$ are identical to the previous ones and are occupied by the K^+ ions.

Such M_6X_{36} clusters have been extensively used in the description of anion excess fluorites by Bevan et al. (17). They were already observed in γ-KYb_3F_{10} by Laval and Frit (5), but a simple description based on a c.c.p. of $UOA_{[12]}$ (neither from $UOA_{[8]}$) was not retained. The use of a c.c.p. of vertex sharing $UOA_{[8]}$ is probably a more convenient way to understand the structure of γ-KYb_3F_{10}. Then, two compounds based on the same packing, $BaCaLu_2F_{10}$(6) and $PbZr_3F_6O_4$(7), are described below using this simplifying method.

For $BaCaLu_2F_{10}$ (S.G.: $Fm3m$, $a = 11.366(2)$ Å, $Z = 8$), a statistical $Ca_{1/3}Lu_{2/3}$ distribution is observed on the $24e$ position. The formula of the $UOA_{[8]}$ formed by six $[Ca_{1/3}Lu_{2/3}F_8]$ antiprisms is $Ca_2Lu_4F_{32}$. This leads to a $[Ca_2Lu_4F_{20}]^{4-}$ three-dimensional network. Every tetrahedral site is occupied by the Ba^{2+} ion ($8c$ position). Octahedral sites of the network — or cuboctahedral anionic cavities — are free. The formulation of this compound is then $\mathbf{Ba_2[Ca_2Lu_4F_{20}]}$, with $\mathbf{Z = 4}$.

A strict order between the O^{2-} and F^- anions is observed in $PbZr_3F_6O_4$ (S.G.: $Fm3m$, $Z = 8$, $a = 10.926(6)$ Å). Anionic cubes (center of the $UOA_{[8]}$) are built up from O^{2-} ions ($32e$), whereas cuboctahedra (center of the $UOA_{[12]}$) are built up from F^- ions ($48f$). Therefore, ZrF_4O_4 antiprisms and $Zr_6O_8F_{24}$ $UOA_{[8]}$ are observed, leading to

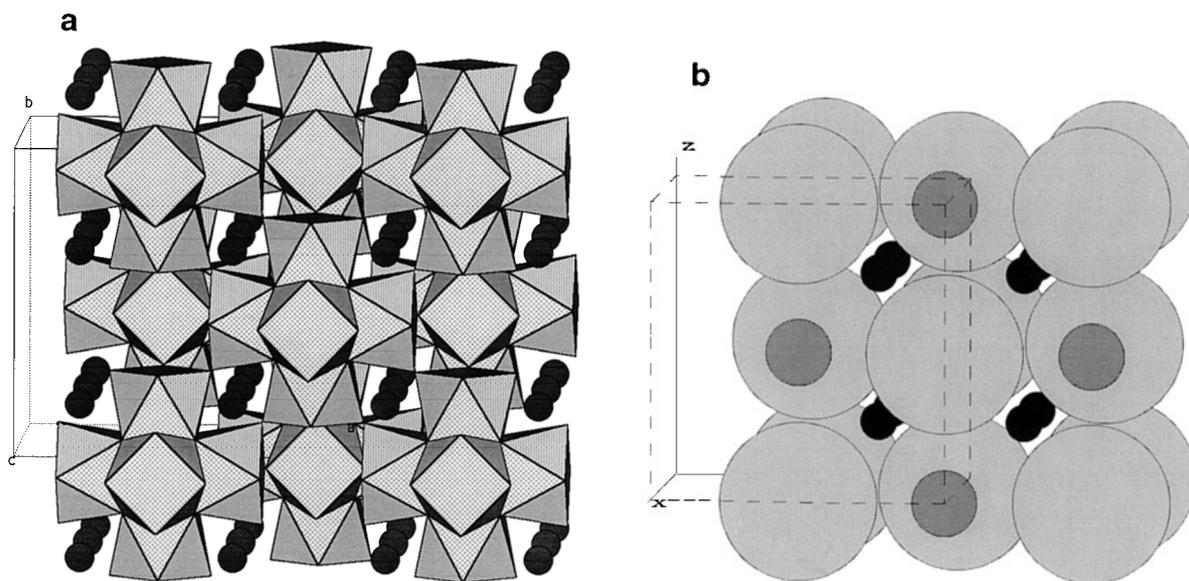**FIG. 3.** Perspective view of γ-KYb_3F_{10} (a) from $UOA_{[8]}$ and (b) from spheres (large and small black circles correspond to octahedral and tetrahedral sites, respectively).
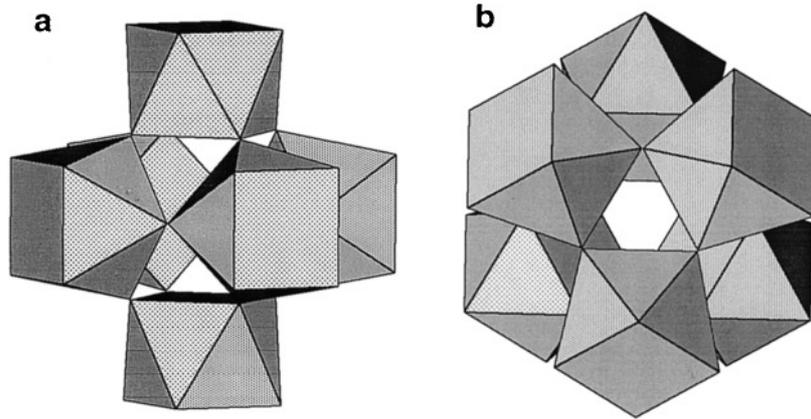
FIG. 4. An UOA$_{[12]}$ M_6X_{36} (a) along a pseudo-fourfold axis and (b) along a pseudo-ternary axis.

a $[Zr_6O_8F_{12}]^{4-}$ 3D network. Every tetrahedral site of the c.c.p. of UOA$_{[8]}$ is occupied by Pb^{2+} ions whose coordination remains tetrahedral ($4O^{2-}$ at 2.61 Å, plus $12F^-$ at 3.02 Å). The formulation of this compound is **$Pb_2[Zr_6O_8F_{12}]$, with $Z = 4$.**

The alloy $Cr_{23}C_6$ (8) (S.G.: $Fm3m$, $a = 10.65$ Å, $Z = 8$) can also be described by a c.c.p. of C_6Cr_{32} UOA$_{[8]}$, leading to a C_6Cr_{20} network. Both tetrahedral sites and octahedral sites — or cubooctahedral cavities — are occupied, respectively, by $Cr_{(2)}$ (8c position) and $Cr_{(1)}$ (4a position). The formula is then **$Cr_2[C_6Cr_{20}]Cr$, with $Z = 4$.** This description seems us more convenient than that based on UOA$_{[12]}$$C_6Cr_{36}$ (18).

The following examples are based on semicompact and noncompact stackings of **UOA$_{[12]}$** or **UOA$_{[8]}$.**

2. STRUCTURES WITH A SEMICOMPACT STACKING OF UOA$_{[12]}$

2.1. AA'A ... Type (Primitive Hexagonal Packing)

The basic polyhedron of $PbZr_6F_{22}O_2$ (5) (S.G.: $P6_3/mmc$, $a = 7.504(4)$ Å, $c = 15.008(7)$ Å, $Z = 2$) is a ZrF_7O antiprism. From our method of description, the UOA$_{[12]}$, $Zr_6F_{30}O_6$ are formed by vertice connections of 6 antiprisms. The central cubooctahedral cavity is built up from 12 F^-. As can be seen in Fig. 5, each UOA$_{[12]}$ is connected by 12 edges to 6 neighboring UOA$_{[12]}$. Thus, compact layers of UOA$_{[12]}$ are observed at $z = 0$ and $z = \frac{1}{2}$. According to the 6_3 axes, these layers are superimposed along c and connected by vertices, leading to a semicompact stacking. The coordination of each UOA$_{[12]}$ is then $1 + 6 + 1$. The
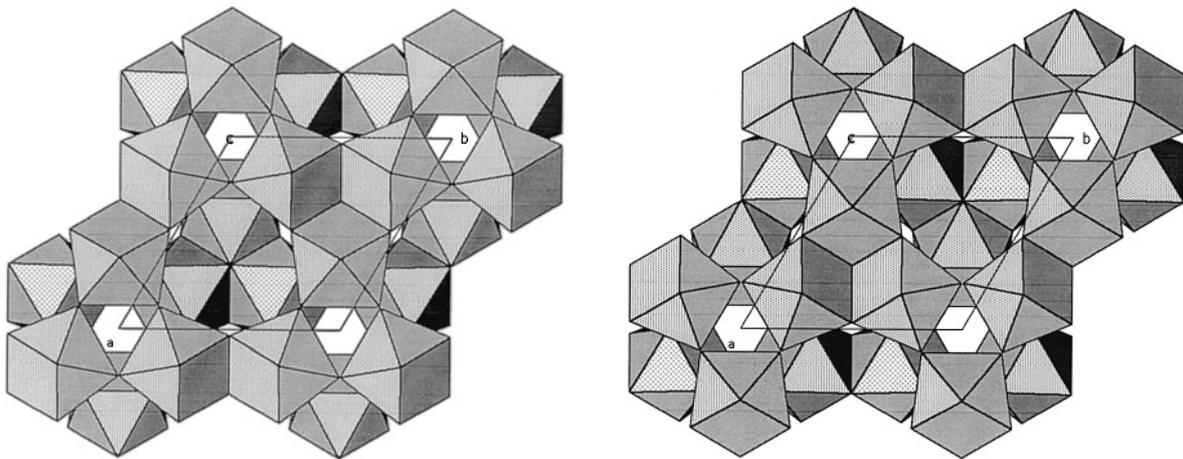

FIG. 5. (001) projection of the compact layers of UOA$_{[12]}$ in $PbZr_6F_{22}O_2$ (left) Layer A ($z = 0$). (Right) Layer A' ($z = \frac{1}{2}$).

coordination of the O^{2-} and F^- anions are equal to 2 and 3, respectively. The formulation of the network is then $Zr_6F_{12}F_{18/2}O_{6/3}$ or $[Zr_6F_{21}O_2]^-$. In this compound, the occupation of the prismatic sites of the network is perfectly ordered. For this reason, a doubling of the c parameter is necessary ($c/a = 2.000$), and this structure corresponds to an AA′A ... type stacking. In the $P6_3/mmc$ space group, the available prismatic sites are situated in the $2d$ ($\frac{1}{3}\frac{2}{3}\frac{3}{4}$, $\frac{2}{3}\frac{1}{3}\frac{1}{4}$) and $2c$ ($\frac{1}{3}\frac{2}{3}\frac{1}{4}$, $\frac{2}{3}\frac{1}{3}\frac{3}{4}$) positions. Pb^{2+} ions only occupy the $2d$ position (see Fig. 6) and are responsible for the doubling of c. The charge equilibrium between the $[Zr_6F_{21}O_2]^-$ network ($Z = 2$) and the Pb^{2+} cations is obtained by the presence of a fluorine anion within the cuboctahedral cavities of the $UOA_{[12]}$. In fact, this fluorine is not located in the center of the cavity, but is statistically distributed on two sites ($4e$). The exact formulation of this compound is then **$Pb[Zr_6F_{21}O_2]F$, with $Z = 2$**.

The same structural type is observed in CsU_6F_{25} (9) (S.G.: $P6_3/mmc$, $a = 8.2424(4)$ Å, $c = 16.412(2)$ Å, $Z = 2$). U_6F_{36} $UOA_{[12]}$ are formed by six UF_8 antiprisms. The three-dimensional network resulting from the AA′A stacking of compact layers of $UOA_{[12]}$ has the formulation $[U_6F_{23}]^+$. Half of the prismatic sites are occupied by the Cs^+ ions. The c parameter is then doubled ($c/a = 1.991$). Two F^-, situated inside the cuboctahedral cavity of the $UOA_{[12]}$, ensure the charge equilibrium. In this case, the distance between the two equivalent positions of fluorine is large enough to allow for a full occupancy of the sites ($d_{F-F} = 2.5$ Å). As Brunton noticed (9), we may consider that these additional F^- are part of the coordination number of U^{4+}, which is then equal to 9. Thus, its coordination polyhedron corresponds to an antiprism capped on a square face. The explicit formulation of CsU_6F_{25} is finally **$Cs[U_6F_{23}]F_2$, with $Z = 2$**.
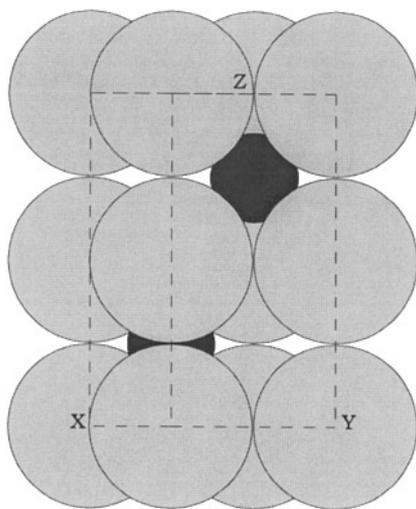
2.2. ABC ... Type

The ninefold coordination of the Th^{4+} ions in the fluoride α-KTh_6F_{25} (10) (S.G.: $R\bar{3}m$, $a = 8.313(2)$ Å, $c = 25.262(4)$ Å, $Z = 3$) is a tricapped trigonal prism of F^-. It is also possible to consider that the coordination of Th^{4+} is a square antiprism capped on a square face, although the distance from the additional anion to the thorium (2.481(7) Å) is smaller than the maximum Th–F distance of the antiprism (2.541(5) Å). Then, α-KTh_6F_{25} can be described with ThF_8 square antiprisms linked by vertices in order to form a Th_6F_{36} $UOA_{[12]}$. As in the examples of $PbZr_6F_{22}O_2$ and CsU_6F_{25}, compact layers of $UOA_{[12]}$, in which each $UOA_{[12]}$ is linked by 12 edges to 6 $UOA_{[12]}$, are observed. With respect to the rhombohedral symmetry, the layers of $UOA_{[12]}$, centered on the $3b$ position (1/3 2/3 1/6, 0 0 1/2, 2/3 1/3 5/6), are connected by vertices according to a semicompact ABC type packing. In this case, the c/a ratio is equal to 3.039. The formulation of the three-dimensional network is $Th_6F_{12}F_{18/2}F_{6/3}$ or $[Th_6F_{23}]^+$ ($Z = 3$). Figure 7 shows the idealized semicompact ABC stacking along c, and a (0 0 1) projection of the compact layers of $UOA_{[12]}$. The K^+ ions (0 0 0) occupy the octahedral sites of the network and are coordinated to 12 fluorine anions. Two F^- situated within the cuboctahedral cavities of the $UOA_{[12]}$ ensure the charge balance. The formulation of this compound is then **$K[Th_6F_{23}]F_2$, with $Z = 3$**.

2.3. ABA ... Type (Body Centered Packing)

From our method of description, Th_6F_{24}, H_2O (11) (S.G.: $14/m$, $a = 9.194$ Å, $c = 11.553$ Å, $Z = 2$) is built up from Th_6F_{36} $UOA_{[12]}$. In this case, each $UOA_{[12]}$ is linked by edges to four neighboring $UOA_{[12]}$. This leads to semicompact layers of $UOA_{[12]}$, at $z = 0$ and $z = 0.5$ (Figs. 8a and 8b). The layers are superimposed along c and connected by
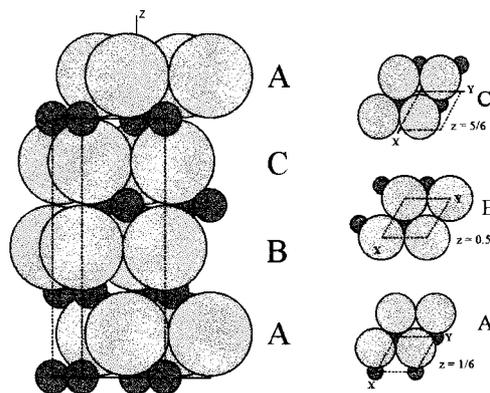
FIG. 6. AA′A stacking in $PbZr_6F_{22}O_2$ (black circles represent Pb^{2+}).

FIG. 7. (Left) Semicompact ABC stacking in α-Th_6F_{25}. (Right) View of the compact layers (black circles represent octahedral sites).
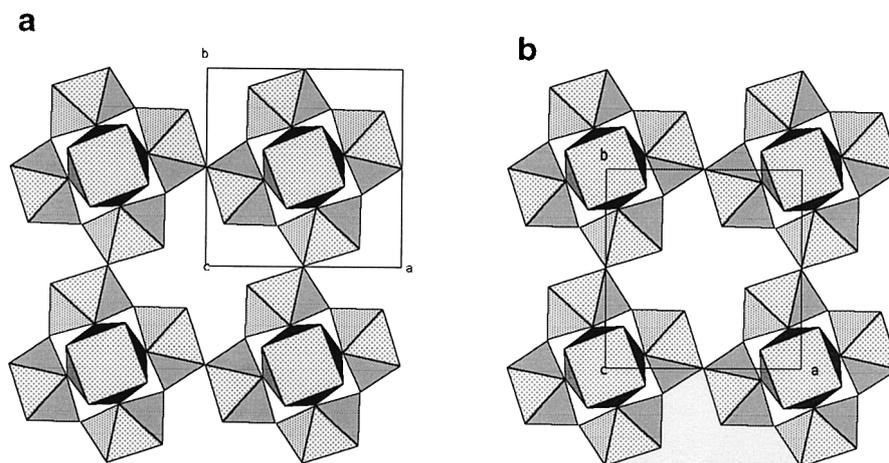
FIG. 8.   (0 0 1) projection of the semicompact layers of $UOA_{[12]}$ in Th_6F_{24},H_2O (a) at $z = 0$ and (b) at $z = 0.5$.

vertices according to an ABA … stacking. The coordination of an $UOA_{[12]}$ is $4 + 4 + 4$ (see Fig. 9). Therefore, a $Th_6F_{12}F_{24/2}$ or $[Th_6F_{24}]^0$ neutral network is created. The formulation is then **$[Th_6F_{24}]H_2O$**, with **$Z = 2$**. The anionic coordination of the water molecules, situated in $0\,0\,0$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ within the layers, is perfectly cubic. This cube is connected by edges to four antiprisms and connected by faces up and down along c to two antiprisms. We may consider that these six antiprisms correspond to another type of $UOA_{[8]}$, whose formulation is M_6X_{40} ($M_6X_8X_{4*6}X_{2*4}$).

3. STRUCTURES WITH A NONCOMPACT STACKING OF $UOA_{[12]}$

3.1. ABC … Type

The compound $Pb_8Y_6F_{32}O$ (12) (S.G.: $R\bar{3}$, $a = 10.817(2)$ Å, $c = 19.942(5)$ Å, $Z = 3$) can be described from

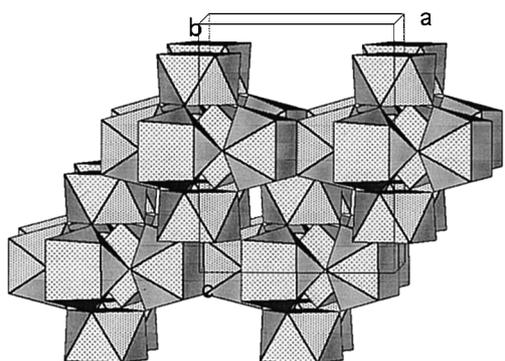**FIG. 9.**   Perspective view near [0 1 0] of the ABA stacking in Th_6F_{24},H_2O.

our method by noncompact layers of Y_6F_{36} $UOA_{[12]}$ centered on the following positions: $\frac{1}{3}\frac{2}{3}\,0.17$, $0\,0\,0.50$, and $\frac{2}{3}\frac{1}{3}\,0.83$. These are exactly the positions of a compact ABC packing, but the $UOA_{[12]}$ are not connected in the layers (see the A, B, and C layers in Fig. 10). As can be seen in Fig. 10d, the $UOA_{[12]}$ share edges in the c direction of the packing. Only one edge is common to two $UOA_{[12]}$. Each $UOA_{[12]}$ is connected to six neighbors (three up + three down) according to an octahedral type. By these connections, a three-dimensional $Y_6F_{12}F_{12}F_{12/2}$ or $[Y_6F_{30}]^{12-}$ network is created ($Z = 3$). The positions of the $Pb^{2+}_{(1)}$ cations ($6c$: $0\,0\,0.26121(3)$) are very close to the positions of the tetrahedral sites of the network: $0\,0\,0.249$. Additional $Pb^{2+}_{(2)}$ cations ($18f$ position, $z = 0.08$) and fluorine anions $F_{(6)}$ ($6c$ position, $z = 0.136$) are situated within the layers. In fact, $F_{(6)}$ anion is coordinated to four Pb^{2+} cations in a tetrahedral way. As can be seen in Fig. 10b, the $[FPb_4]^{7+}$ tetrahedra occupy the available space of the noncompact layers of $UOA_{[12]}$ (the tetrahedra are not connected to the layers). However, the resulting $[(FPb_4)_2Y_6F_{30}]^{2+}$ network is not balanced. The charge equilibrium is obtained by the presence of O^{2-} anions ($3a$: $0\,0\,0$) situated in the octahedral sites of the network of $UOA_{[12]}$, that is, between two successive layers. The coordination of this O^{2-} anion is made of eight fluorine anions according to a cubic symmetry. The detailed formula of $Pb_8Y_6F_{32}O$ is finally **$(FPb_4)_2[Y_6F_{30}]O$**, with **$Z = 3$**.

The same ABC stacking of noncompact layers of $UOA_{[12]}$ can be used for the description of $Nd_{14}Cl_{32}O$ (13) (S.G.: $R\bar{3}$, $a = 12.980$ Å, $c = 24.835$ Å, $Z = 3$). Indeed, $[ClNd_4^{II}]^{7+}$ tetrahedra are situated within a $[Nd_6^{III}Cl_{30}]^{12-}$ network. In this compound, the O^{2-} anions are reported to be situated within the cuboctahedral cavities of the $UOA_{[12]}$. The detailed formula of this compound is **$(ClNd_4)_2[Nd_6Cl_{30}]O$**, with **$Z = 3$**.

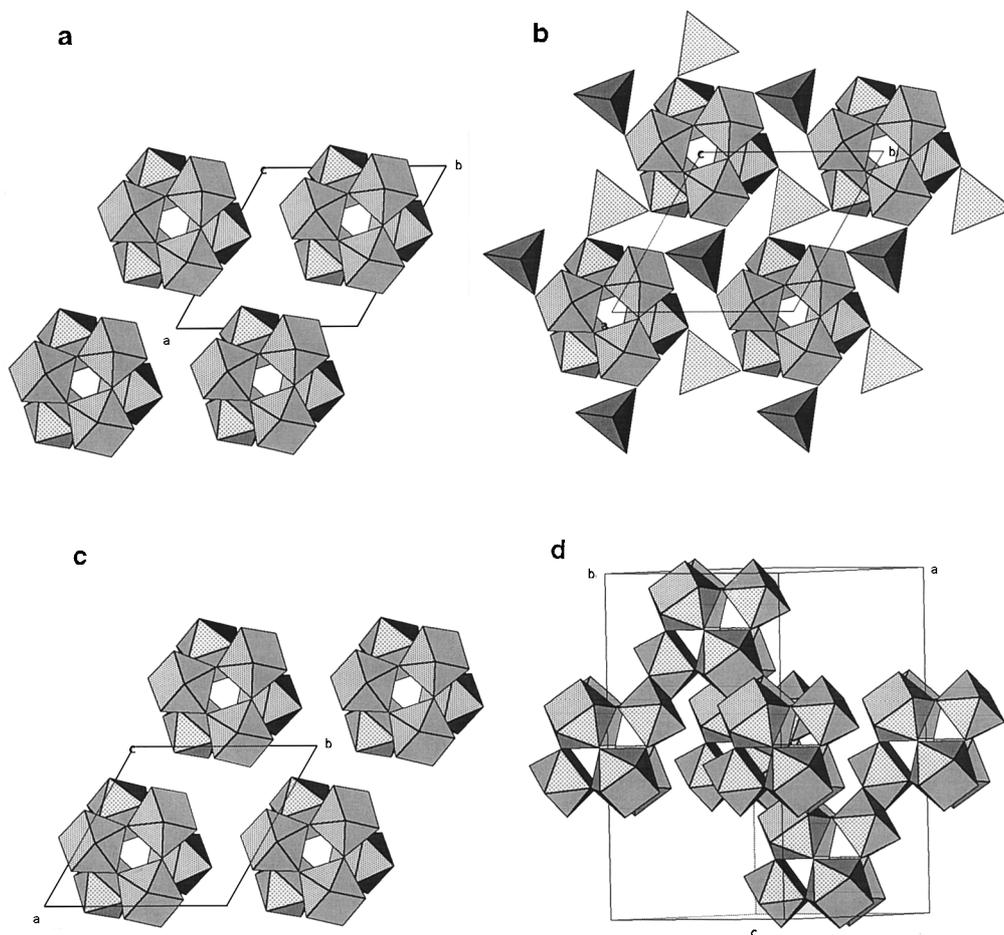**FIG. 10.** (0 0 1) projections of $Pb_8Y_6F_{32}O$. (a) Layer A at $z = 0.17$. (b) Layer B at $z = \frac{1}{2}$, with the $(FPb_4)^{7+}$ tetrahedra. (c) Layer C at $z = 0.83$. (d) View of the ABC stacking near [1 1 0].

3.2. Diamond Type

$(H_3O)Yb_3F_{10},H_2O$ is the main example from which has been elaborated our method of description of complex structures from UGP (see the preceeding publication). It can be simply described by a diamond network of Yb_6F_{32} UOA$_{[8]}$ leading to a Yb_6F_{20} network. The hydronium ions and the water molecules are situated within the tunnels. The detailed formulation is $(H_3O)_2[Yb_6F_{20}],2H_2O$, with $Z = 8$.

The chlorofluoride $Sr_{10}Al_2F_{25}Cl$ (14) (S.G.: $Fd\overline{3}m$, $a = 16.4209(3)$ Å, $Z = 8$) provides an example of nonconventional UOA$_{[12]}$. Indeed, the coordination of $Sr_{(2)}$ is a distorted antiprism having only one square face. Two triangular faces substitute for the second square face. However, 6 distorted antiprisms are connected by vertices around a cuboctahedral cavity made of 12 fluorine anions. The resulting Sr_6F_{36} UGP can be called UOA$_{[12]}$ on the condition that the letter A stands for "distorted antiprisms."

A chlorine anion is situated within the cuboctahedral cavities of the UOA$_{[12]}$. The position of Cl^- (8a: 0 0 0, $\frac{3}{4}$ $\frac{1}{4}$ $\frac{3}{4}$) clearly indicates that the structure is a diamond type stacking of UOA$_{[12]}$. Each UOA$_{[12]}$ is surrounded by 4 neighboring UOA$_{[12]}$ in a tetrahedral way. Two neighboring UOA$_{[12]}$ share six vertices by six edges. Each distorted SrF_8 antiprism has two free vertices. The formulation of the network is $Sr_6F_{6/2*4}F_{12}$ or Sr_6F_{24}, with $Z = 8$. Eight tetrahedral sites of the diamond stacking (position 8b: $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$, $\frac{1}{4}$ $\frac{3}{4}$ $\frac{1}{4}$) are occupied by additional F^- anions. Their coordination is made of 4 $Sr_{(1)}^{2+}$, leading to $(FSr_4)^{7+}$ tetrahedra. The Al^{3+} cations are situated in the center of an octahedron of F^- anions generated by the Sr_6F_{24} network. $Sr_{10}Al_2F_{25}Cl$ is then a diamond stacking of distorted Sr_6F_{36} UOA$_{[12]}$ whose cuboctahedral cavities are occupied by a chlorine anion. All the tetrahedral sites of the network are occupied by FSr_4 tetrahedra. The detailed formulation of this compound is $(FSr_4)[Sr_6F_{24}]Al_2Cl$, with $Z = 8$.

TABLE 1
Characteristics of the Structures Described from Simple Stackings of UGP (UOA[8] or UOA[12])

Compound	Basic polyhedron	UGP	Layers	Type of stacking	Network	Position of the cations	Available sites [12]	[8]	[6]	Formulation
$H_3OYb_3F_{10}$,H_2O $Fd3m$ $Z = 16$ $a = 15.3263(2)$ Å	YbF_8 antiprism	Yb_6F_{32} UOA[8]		Diamond	$[Yb_6F_{20}]^{2-}$ $Z = 8$	H_3O^+: center of the hexagons H_2O: in the cages	×	□	×	$[M_6X_{20}]$ $(H_3O)_2[Yb_6F_{20}],2H_2O$ $Z = 8$
β-KYb_3F_{10} $P6_3mc$ $Z = 4$ $a = 8.067(2)$ Å $c = 13.203(4)$ Å	YbF_8 antiprism	Yb_6F_{32} UOA[8]	Compact layers of UOA[8]	h.c.p (ABA) $c/a = 1.637$	$[Yb_6F_{20}]^{2-}$ $Z = 2$	$2 K^+$: in half of the tetrahedral sites $2 K^+$: near the tetrahedral sites	×	□	×	$[M_6X_{20}]$ $K_2[Yb_6F_{20}]$ $Z = 2$
$Zr_3F_8O_2$ $P6_3mc$ $Z = 4$ $a = 7.771(5)$ Å $c = 12.49(1)$ Å	ZrF_6O_2 antiprism	$Zr_6(F_4O_4)F_{24}$ UOA[8]	Compact layers of UOA[8]	h.c.p. (ABA) $c/a = 1.628$	$[Zr_6O_4F_{16}]^0$ $Z = 2$		×	□	×	$[M_6X_{20}]$ $[Zr_6(F_4O_4)F_{12}]$ $Z = 2$
γ-KYb_3F_{10} $Fm3m$ $Z = 8$ $a = 11.431$ Å	YbF_8 antiprism	Yb_6F_{32} UOA[8] or Yb_6F_{36} UOA[12]	Compact layers of UOA[8]	c.c.p. (ABC)	$[Yb_6F_{20}]^{2-}$ $Z = 4$	$8K^+$: in the tetrahedral sites	□	□	×	$[M_6X_{20}]$ $K_2[Yb_6F_{20}]$ $Z = 4$
$BaCaLu_2F_{10}$ $Fm3m$ $Z = 8$ $a = 11.366(2)$ Å	$Ca_{1/3}Lu_{2/3}F_8$ antiprism	$Ca_2Lu_4F_{32}$ UOA[8] or $Ca_2Lu_4F_{36}$ UOA[12]	Compact layers of UOA[8]	c.c.p.	$[Ca_2Lu_4F_{20}]^{4-}$ $Z = 4$	$8 Ba^{2+}$: in the tetrahedral sites	□	□	×	$[M_6X_{20}]$ $Ba_2[(Ca_2Lu_4)F_{20}]$ $Z = 4$
$PbZr_3F_6O_4$ $Fm3m$ $Z = 8$ $a = 10.926(6)$ Å	ZrF_4O_4 antiprism	$Zr_6O_8F_{24}$ UOA[8] or $Zr_6F_{12}O_{24}$ UOA[12]	Compact layers of UOA[8]	c.c.p.	$[Zr_6O_8F_{12}]^{4-}$ $Z = 4$	$8 Pb^{2+}$: in the tetrahedral sites	□	□	×	$[M_6X_{20}]$ $Pb_2[Zr_6O_8F_{12}]$ $Z = 4$
$Cr_{23}C_6$ $Fm3m$ $Z = 8$ $a = 10.65$ Å	CCr_8 antiprism	C_6Cr_{32} UOA[8] or C_6Cr_{36} UOA[12]	Compact layers of UOA[8]	c.c.p.	$[C_6Cr_{20}]$ $Z = 4$	$8 Cr$: in the tetrahedral sites	● 4 Cr	□	×	$[M_6X_{20}]$ $Cr_2[C_6Cr_{20}]Cr$ $Z = 4$
$PbZr_6F_{22}O_2$ $P6_3/mmc$ $Z = 2$ $a = 7.504(4)$ Å $c = 15.008(7)$ Å	ZrF_7O antiprism	$Zr_6F_{30}O_6$ UOA[12]	Compact layers of UOA[12]	AA'A $c/a = 2.000$	$[Zr_6F_{21}O_2]^-$ $Z = 2$	Pb^{2+}: in half of the prismatic sites	● 1 F^-	×	×	$[M_6X_{23}]$ $Pb[Zr_6F_{21}O_2]F$ $Z = 2$
CsU_6F_{25} $P6_3/mmc$ $Z = 2$ $a = 8.2424(4)$ Å $c = 16.412(2)$ Å	UF_8 antiprism	U_6F_{36} UOA[12]	Compact layers of UOA[12]	AA'A $c/a = 1.991$	$[U_6F_{23}]^+$ $Z = 2$	Cs^+: in half of the prismatic sites	● 2 F^-	×	×	$[M_6X_{23}]$ $Cs[U_6F_{23}]F_2$ $Z = 2$
α-KTh_6F_{25} $R\bar{3}m$ $Z = 3$ $a = 8.313(2)$ Å $c = 25.262(4)$ Å	ThF_8 antiprism	Th_6F_{36} UOA[12]	Compact layers of UOA[12]	ABC semi-compact $c/a = 3.039$	$[Th_6F_{23}]^+$ $Z = 3$	K^+: in the octahedral sites	● 2 F^-	×	×	$[M_6X_{23}]$ $K[Th_6F_{23}]F_2$ $Z = 3$
Th_6F_{24}, H_2O $I4/m$ $Z = 2$ $a = 9.194$ Å $c = 11.553$ Å	ThF_8 antiprism	Th_6F_{36} UOA[12]	Semi-compact layers of UOA[12]	ABA	$[Th_6F_{24}]^0$ $Z = 2$		□	● 2 H_2O	×	$[M_6X_{24}]$ $[Th_6F_{24}]H_2O$ $Z = 2$
$Sr_{10}Al_2F_{25}Cl$ $Fd3m$ $Z = 8$ $a = 16.4209(3)$ Å	SrF_8 distorted antiprism	Sr_6F_{36} UOA[12]		Diamond	$[Sr_6F_{24}]^{2-}$ $Z = 8$	$2 Al^{3+}$ in octahedral sites: $[Al_2Sr_6F_{24}]^{6-}$ F^- in tetrahedral sites $(FSr_4)^{7+}$ tetraedra	● Cl^-	×	● 2 Al^{3+}	$[M_6X_{24}]$ $(FSr_4)[Sr_6F_{24}]Al_2Cl$ $Z = 8$
$Pb_8Y_6F_{32}O$ $R\bar{3}$ $Z = 3$ $a = 10.817(3)$ Å $c = 19.942(5)$ Å	YF_8 antiprism	Y_6F_{36} UOA[12]	Non-compact layers of UOA[12]	ABC	$[Y_6F_{30}]^{12-}$ $Z = 3$	$8 Pb^{2+} + 2F^-$ in the layers: two $[FPb_4]^{7+}$ tetrahedra	□	● O^{2-}	×	$[M_6X_{30}]$ $(FPb_4)_2[Y_6F_{30}]O$ $Z = 3$
$Nd_{14}Cl_{32}O$ $R\bar{3}$ $Z = 3$ $a = 12.980$ Å $c = 24.835$ Å	$Nd^{III}F_8$ antiprism	$Nd_6^{III}F_{36}$ UOA[12]	Non-compact layers of UOA[12]	ABC	$[Nd_6Cl_{30}]^{2-}$ $Z = 3$	$(ClNd_4^{II})^{7+}$ tetrahedra	● O^{2-}	□	×	$[Nd_6X_{30}]$ $(ClNd_4)_2[Nd_6Cl_{30}]O$ $Z = 3$

Note: Available sites: [12], anionic cuboctahedron; [8], anionic cube; [6], anionic octahedron. Codes: ●, occupied site; □, vacant site; ×, does not exist.
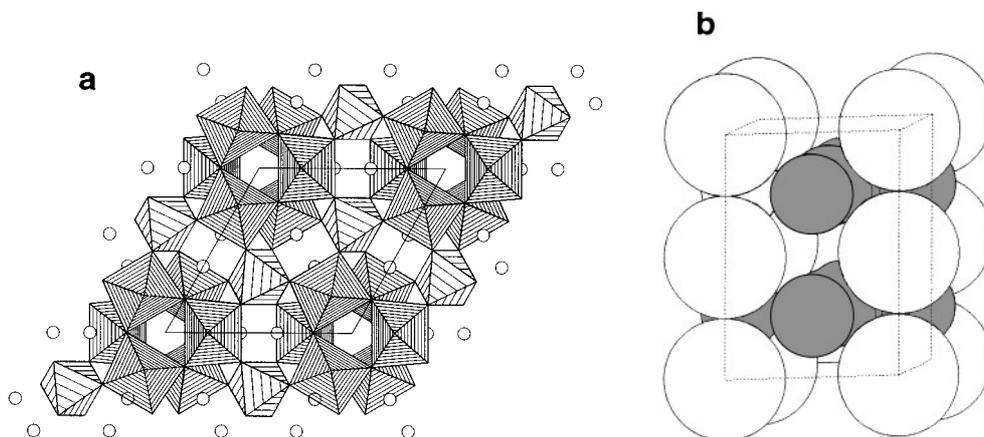
FIG. 11. (0 0 1) projection of $K_3Nb_8O_{21}$. (a) The $UOO_{[6]}$ layers are noncompact (additional NbO_6 octahedra are located in vacant space between the $UOO_{[6]}$). (b) View of the AA'A stacking along c (vacant sites are shown by black circles).

4. A FURTHER EXAMPLE

Our method of description can be extended to other types of UGP. For example, from six MX_6 octahedra connected by vertices and edges, an octahedral unit of octahedra is created whose center is an anionic octahedron. In agreement with our preceding notations, this M_6X_{24} block can be called $UOO_{[6]}$. This kind of UGP is observed in the oxide $K_3Nb_8O_{21}$ (S.G.: $P6_3/mcm$, $a = 9.153(4)$ Å, $c = 12.066(4)$ Å, $Z = 2$), which is a member of the $A_3M_8O_{21}$ family (A = Ba, K; M = Nb, Ti) (15). The basic polyhedron is an $[NbO_6]$ octahedron, leading to a $[Nb_6O_{24}]$ $UOO_{[6]}$. Non compact layers of $UOO_{[6]}$ are observed perpendicular to the c axis, as can be seen in Fig. 11a. These layers are connected by vertices along c and superimposed according to an AA'A type stacking. A $[Nb_6O_{21}]$ network built up from infinite chains of $UOO_{[6]}$ is observed. The K^+ ions are found near the fourfold coordination sites situated in $\frac{1}{2}$ 0 $\frac{1}{4}$ (see Fig. 11b). For geometrical reasons, their position is $x \approx 0.6$ 0 $\frac{1}{4}$ (6g), and their anionic coordination becomes $10 + 3$ (tricapped pentagonal prism). The two other Nb atoms are situated in an anionic octahedral site generated by a vacant space between the $UOO_{[6]}$. It must be noted that the central octahedral cavity of the $UOO_{[6]}$ is not occupied. The explicit formulation of this compound is then $K_3[Nb_6O_{21}]Nb_2$, with $Z = 2$.

5. CONCLUSION

Three points can be retained from our description of complex structures by means of UGP.

The first is that our method gives a simplifying and didactic view of complex structures. The required conditions are to define the UGP (from polyhedra connections) and to establish the type of stacking of layers of UGP (except for diamond). A structure description is given by an explicit formulation "counterions[network]additional ions." Table 1 summarizes the given examples; the UGP are mainly $UOA_{[8]}$ or $UOA_{[12]}$ built up from MX_8 antiprisms.

The second point concerns the possibility of using the formulation as a predictive tool for synthesis experiments. Some experiments have already been performed in the case of $Cs[U_6F_{23}]F_2$. Indeed the substitution $Cs^+ + U^{4+} \rightarrow Ba^{2+} + Ln^{3+}$ leads to the family $Ba[U_5LnF_{23}]F_2$ (Ln = La to Lu) (16). Obviously the neutral network $[U_5LnF_{23}]$ could exist without additional charge, but the usual ninefold coordination of U^{4+} would not be reached. Perhaps the presence of a chlorine ion in the cuboctahedral cavity, instead of two fluorine anions, would be sufficient to stabilize the surroundings of the uranium; the formulation of the new phase would be $Cs[U_5LnF_{23}]Cl$. From this point of view, numerous syntheses may be attempted.

Finally, the third point is related to the idea that solid state compounds could obey a scale law. For a given stacking, the unit cell parameters depend only on the size of the elementary UGP. This idea is well illustrated for the diamond type stacking, in the compounds C(diamond), β-SiO$_2$ (ideal), $(H_3O)Yb_3F_{10},H_2O$, and $Sr_{10}Al_2F_{25}Cl$. For these species, the basic units are successively the carbon atom [C], the tetrahedron [SiO$_4$], the $UOA_{[8]}$ [Yb$_6$F$_{32}$], and the $UOA_{[12]}$ [Sr$_6$F$_{36}$]. Similarly, the cubic cell parameters are respectively 3.57, 7.16, 15.33, and 16.42 Å.

As a general conclusion, we can say that the use of UGP to describe complex structures is a possible method to state how simple "nature" can really be.

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