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Structural principles for minerals and inorganic compounds containing anion-centered tetrahedra

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ABSTRACT

Several minerals and inorganic compounds contain (XA_4) tetrahedra, with anions, X (O^{2-}, N^{3-}, and F^-), as central atoms and cations, A (Cu^{2+}, Zn^{2+}, Pb^{2+}, Bi^{3+}, REE^{3+}, etc.), as ligands. These tetrahedra are well defined in these crystal structures because the bond valences between A and X are essentially higher than the bond valences between A and atoms from other structural units. According to their size, anion-centered tetrahedra may be subdivided into large and small tetrahedra, formed from cations with ionic radii near to 1.0 Å (e.g., Pb^{2+}, Bi^{3+}, and REE^{3+}) and 0.5–0.7 Å (e.g., Cu^{2+} and Zn^{2+}), respectively. The small anion-centered tetrahedra prefer to link through corners, whereas the large tetrahedra prefer to link through edges. When the tetrahedra are built from both "small" and "large" cations, "small" cations prefer to be corners shared between lesser numbers of tetrahedra and not involved in linking tetrahedra via edges. The general crystal-chemical formula of minerals and compounds containing anion-centered tetrahedra may be written as $A'_k[X_nA_m][A_pX_q]X'_l$, where $[X_nA_m]$ (usually $n \le m$) is a structural unit based on anion-centered tetrahedra (ACT) and $[A_pX_q]$ ($p < q$) is a structural unit based on cation-centered polyhedra (CCP). A' is a cation that does not belong to anion- or cation-centered polyhedra; it is usually an interstitial cation such as an alkali metal; X' is an interstitial anion such as halide or S^{2-}. Structures containing both ACT and CCP units may be ordered according to the values of their dimensionality. In structures without CCP units, an important role is played by large interstitial anions that link finite ACT units, chains, or layers into three-dimensional structures or fill cavities in ACT frameworks.

INTRODUCTION

Minerals are commonly viewed in terms of cation polyhedra; yet, many simple important oxide mineral types are composed entirely of O-centered tetrahedra (alumina-hematite; fluorite-related oxides such as cerianite, thorianite, and bixbyite; copper oxides such as cuprite, tenorite, and paramelaconite; lead oxides such as litharge and massicot; wurtzite-structure oxides such as bromellite and zincite, etc.; O'Keeffe and Bovin 1978; O'Keeffe and Hyde 1985, 1996; Hyde and Andersson 1989; Krivovichev et al. 1998a). Structural units based on (XA_4) anion-centered tetrahedra differ from those based on (AX_4) cation-centered ones (e.g., silicates) in that they may link through edges as well as through corners. This possibility gives rise to many polyions that may be classified on the basis of extended systematics of silicates proposed by Liebau (1982, 1985). Using the arguments by Krivovichev (1997) and Krivovichev et al. (1997), oxocentered tetrahedral polyions were subdivided into 63 structurally distinct types (Krivovichev et al. 1998a), at least one-half of which occur in minerals. Schleid (1996) described seven structural units consisting of N-centered tetrahedra, and two additional units may be added to this list from work of Lulei and Corbett (1995) and Braun et al. (1996). However, these reviews focused on only the linkage topology of anion-centered tetrahedral units, and not on their relations with other units in a structure. A description of crystal structures in terms of anion coordination based on purely geometric aspects was developed by O'Keeffe and Hyde (1985) with emphasis on the arrangement of cations and by Brese and O'Keeffe (1995) for the description of inorganic nitrides. The primary motivation of the present paper is to use bond-valence theory to examine the rules of construction of structures with (XA_4) tetrahedra. The second motivation is that oxocentered metal polycations play a role in the transport processes of metals in gases and aqueous solutions (Hilpert 1990; Boldyrev et al. 1995; Henry et al. 1991; Rouse and Peacor 1994; Grimes et al. 1995), and it is possible that condensation of these polycations results in minerals with crystal structures containing well-defined oxocentered tetrahedra.

ANION-CENTERED TETRAHEDRA AS INDEPENDENT STRUCTURAL SUBUNITS

Consideration from the viewpoint of bond-valence theory

The strength of X-A bonds in anion-centered (XA_4) tetrahedra can be understood in terms of bond-valence theory (Brown 1981; Brese and O'Keeffe 1991). Table 1 gives the bond-length and bond-valence analysis of minerals containing O atoms belonging to oxyanions (TO_q) (T = Se, S, Cr, V, As; q = 3, 4) and additional O atoms; these O atoms are designated

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TABLE 1. Selected bond lengths (Å) and bond valences (vu) for minerals containing oxocentered (OA_4) tetrahedra (A = Cu, Pb). O_a: additional oxygen atoms; O_T: oxygen atoms involving in strong cation-centered complexes (T = Se, S, Cr, V, As).

Mineral	Formula	O_a–A characteristics			O_T–A characteristics		
		< O_a–A >	Dispersion	bv	< A–O_T >	Dispersion	bv
Georgbokiite*	$Cu_5O_2(SeO_3)_2Cl_2$	1.95	1.93–1.98	0.48	2.00	1.94–2.05	0.42
Kamchatkite†	$KCu_3OCl(SO_4)_2$	1.92	1.86–1.98	0.52	2.01	1.93–2.08	0.41
Dolerophanite‡	$Cu_2O(SO_4)$	1.92	1.88-2.00	0.52	1.99	1.91-2.07	0.43
Euchlorine§	$NaKCu_3O(SO_4)_3$	1.93	1.91-1.94	0.51	1.97	1.92-2.03	0.45
Fedotovite#	$K_2Cu_3O(SO_4)_3$	1.93	1.92–1.96	0.51	1.97	1.93-2.03	0.45
Phoenicochroite||	$Pb_2O(CrO_4)$	2.30	2.28–2.31	0.60	2.78	2.46-2.93	0.16
Kombatite**	$Pb_{19}(VO_4)_2O_9Cl_4$	2.32	2.18–2.59	0.57	2.77	2.36-3.10	0.17
Lanarkite§§	$Pb_2O(SO_4)$	2.30	2.27-2.33	0.60	2.66	2.46-2.85	0.23
Freedite††	$Pb_8Cu(AsO_3)_2O_3Cl_5$	2.40	2.18-2.57	0.46	2.57	2.34-2.89	0.29

* Krivovichev et al. 1999b.
† Varaksina et al. 1990.
‡ Effenberger 1985.
§ Scordari and Stasi 1990.
\# Starova et al. 1991.
|| Williams et al. 1970.
** Cooper and Hawthorne 1994.
§§ Sahl 1970.
†† Pertlik 1987.

as O_T and O_a, respectively. The strength of O_a–A bonds is usually higher than that of O_T–A bonds. The difference in these values is particularly great when A = Pb^{2+}.

Hawthorne (1983, 1986, 1994) proposed to order crystal structures hierarchically according to the polymerization of coordination polyhedra with higher bond valences. The application of this principle to structures under consideration allows us to treat anion-centered tetrahedra as independent structural subunits.

We define an anion-centered tetrahedral unit as one based on tetrahedra having anions, X, as centers, and metal atoms, A, as ligands, such that X-A bond valences are higher than bond valences between A and atoms from other structural units. We use "CCP unit" here to indicate structural units based on strong cation-centered polyhedra defined in a similar way (e.g., oxyanions).

Size classification

Cations forming (XA_4) anion-centered tetrahedra may be subdivided into two classes according to their ionic radii, r_A (Shannon 1976): (1) small cations with r_A = 0.5–0.7 Å: e.g., Cu^{2+}, Zn^{2+}, rarely Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, and Al^{3+} in octahedral coordination and (2) large cations with $r_A \geq 1.0$ Å: e.g., Pb^{2+}, Sn^{2+}, REE^{3+}, and Bi^{3+}. Tetrahedra formed by cations from both classes simultaneously are designated as mixed.

Small and large tetrahedra are characterized by the X-A distances, which are listed in Table 2 for X = O^{2-} and N^{3-}. The X-X separations are given for the corner, edge, and face sharing between undistorted (XA_4) tetrahedra. Owing to the greater distances, repulsive forces between the centers of large tetrahedra are considerably lower than those between small tetrahedra. Face-sharing of two tetrahedra leads to very close contact between the central anions, and therefore is next to impossible where X is N^{3-} or O^{2-}; however, it can occur in fluorine-centered tetrahedra (Krivovichev et al. 1998b).

TABLE 2. Geometrical characteristics for linkage of undistorted anion-centered (XA_4) tetrahedra via corner, edge and face

X	A	X – A (Å)	X–X (Å) for two (XA_4) tetrahedra sharing		
			corner	edge	face
O^{2-}	Cu^{2+}, Zn^{2+}	1.90–2.00	3.80–4.00	2.20–2.32	1.27–1.34
O^{2-}	Pb^{2+}, Sn^{2+}, REE^{3+}	2.20–2.40	4.40–4.80	2.55–2.78	1.47–1.61
N^{3-}	REE^{3+}	2.20–2.50	4.40–5.00	2.55–2.90	1.47–1.68

Linkage topology

Analysis of the topology of oxocentered tetrahedral units leads to some empirical rules (Krivovichev et al. 1998a) that may be complemented by the proposed size classification of anion-centered tetrahedra. (1) Anion-centered (XA_4) tetrahedra may link with each other via edges (preferable for large tetrahedra) and via corners (preferable for small tetrahedra). (2) The maximum number of tetrahedra sharing a common corner is eight. (3) The maximum number of tetrahedra sharing a common edge is three, but usually is one (no linkage) or two.

As a consequence of the first rule, the following statement is valid: if a structural unit is composed of mixed (XA_4) tetrahedra, small cations prefer to link (a few) tetrahedra via corners than via edges. This statement is illustrated by Figure 1. The large Bi atoms participate only in linkage of tetrahedra via edges, whereas the small Cu atoms link tetrahedra via corners rather than via edges. As both edge and corner sharing increase the repulsive forces between the central anions, large cations are always preferred to the small ones anytime a linkage occurs, especially in the case of edge sharing (cf. Table 2).

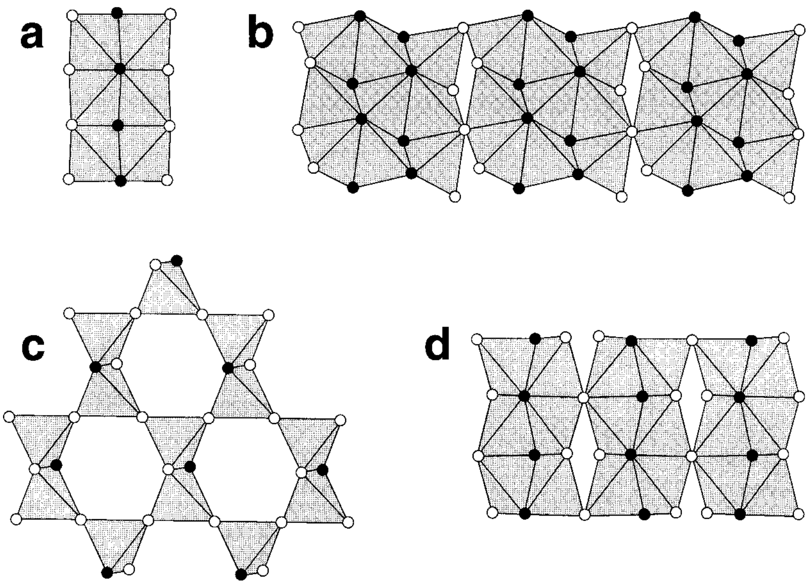
Structural units in minerals and compounds with anion-centered tetrahedra

In accord with Lima-de-Faria et al. (1990) and Smith et al. (1998), the following crystal-chemical formula may be proposed for compounds with anion-centered tetrahedra: $A'_k[X_nA_m][A_pX_q]X'_l$, where A' is a cation that does not belong either to anion- or to cation-centered polyhedra; usually an interstitial cation such as an alkali metal; $[X_nA_m]$ (usually $n \leq m$) is an ACT unit and $[A_pX_q]$ ($p < q$) is a CCP unit; X' is an interstitial anion such as halide or S^{2-}. To classify such minerals and compounds, we consider structures with and without CCP units separately.

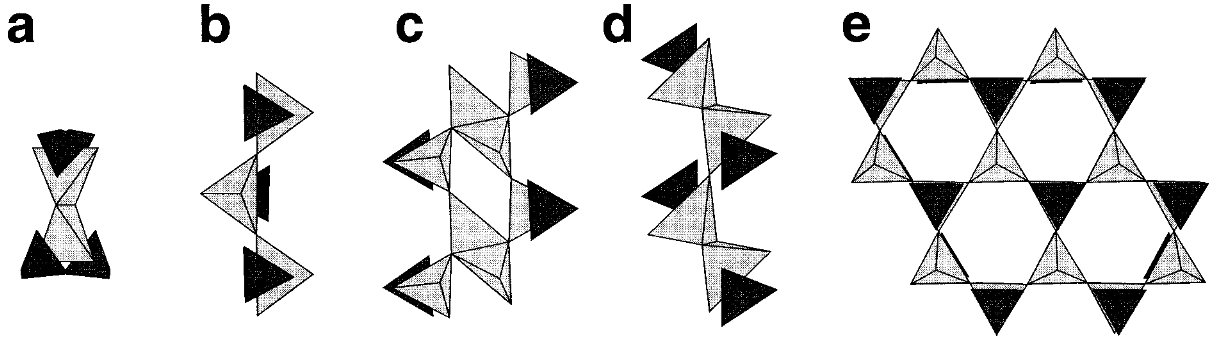
STRUCTURES WITH CCP UNITS

Systematics

This group is classified via the dimensionality (*D*) of the ACT and CCP units. Because *D* takes values from 0 to 3, there exist only 4 × 4 = 16 possible groups. Examples of the miner-



← **FIGURE 1.** Structural units based on the mixed (OA_4) oxocentered tetrahedra (A = Bi and Cu, shown as filled and unfilled circles, respectively): (**a**) $^1_\infty[O_2BiCu_2]$ double chain from $[BiCu_2O_2](PO_4)$ (Abraham et al. 1994); (**b**) $^2_\infty[O_6Bi_4Cu_3]$ layer from $[Cu_3Bi_4O_6](VO_4)_2$ (Deacon et al. 1994); (**c**) $^2_\infty[O_2BiCu_3]$ layer from the structure of francisite, $[Cu_3BiO_2](SeO_3)_2Cl$ (Pring et al. 1990); (**d**) $^2_\infty[O_4Bi_2Cu_3]$ layer from $A'_2[Bi_2Cu_3O_4](AsO_4)_2{\cdot}nH_2O$ (A' = Na, K; n = 1, 2) (Effenberger and Miletich 1995).



↑ **FIGURE 2.** "Face-to-face" relationships between cation-centered groups (dark) and anion-centered tetrahedral units (light) in crystal structures: (**a**) double $[O_2Cu_6]$ tetrahedra and (SO_4) groups in fedotovite, $K_2[Cu_3O](SO_4)_3$ (Starova et al. 1991) and euchlorine, $NaK[Cu_3O](SO_4)_3$ (Scordari and Stasi 1990); (**b**) single $^1_\infty[O_2Cu_6]$ chains and tetrahedral groups in kamchatkite, $K[Cu_3O](SO_4)_2Cl$ (Varaksina et al. 1990) and chloromenite, $Cu_3[Cu_6O_2](SeO_3)_4Cl_6$ (Krivovichev et al. 1998c); (**c**) double $^1_\infty[O_2Cu_5]$ chains and (VO_4) groups in stoiberite, $[Cu_5O_2](VO_4)_2$ (Shannon and Calvo 1973; Birnie and Hughes 1979); (**d**) single $^1_\infty[O_2Cu_5]$ chains and (SeO_3) groups in georgbokiite, $[Cu_5O_2](SeO_3)_2Cl_2$ (Galy et al. 1979; Krivovichev et al. 1999b); (**e**) $^2_\infty[O_2Cu_5]$ layers and (VO_4) groups in averievite, $Cu_5O_2(VO_4)_2{\cdot}MCl$ (M = K, Rb, Cs) (Starova et al. 1997).

als and/or inorganic compounds are given in Table 3. Some groups have not been observed.

The ACT and CCP units adapt to attain energetically advantageous structural configurations. We now describe the main principles of adaptation mechanisms for the various groups.

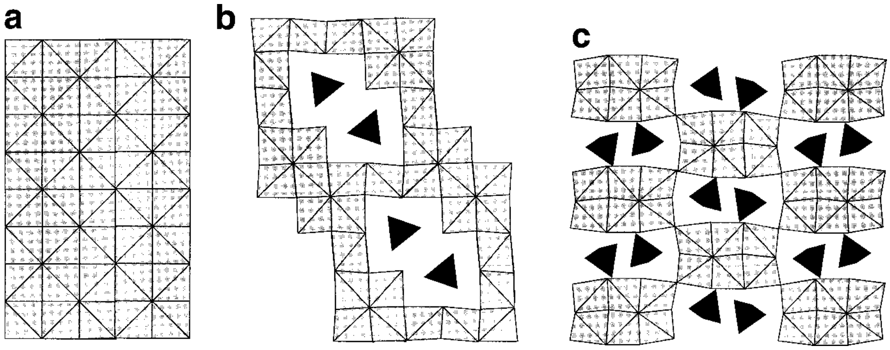
$D_{CCPU} < D_{ACTU}$ and $D_{CCPU} = D_{ACTU} = 0$

The "face-to-face" principle. This principle involves structures with single (AO_q) cation-centered polyhedra with triangular O-O-O faces (q = 3 or 4) and ACT units based on small (XA_4) tetrahedra. It was firstly recognized by Starova et al. (1997) for averievite, $Cu_5O_2(VO_4)_2{\cdot}MCl$ (M = K, Rb, and Cs), and is based on the approximate commensurability between the O-O distances in the (AO_q) groups (2.4–2.8 Å) and A-A distances in small (XA_4) tetrahedra (2.9–3.2 Å). This commensurability allows (AO_q) polyhedra to attach to faces of (XA_4) tetrahedra (Fig. 2). In such minerals, tetrahedral or trigonal pyramidal oxyanions [(SO_4), (VO_4), (SeO_3)] are attached to the bases of (OCu_4) tetrahedra in agreement with the "face-to-face" principle (for details see Krivovichev et al. 1999a).

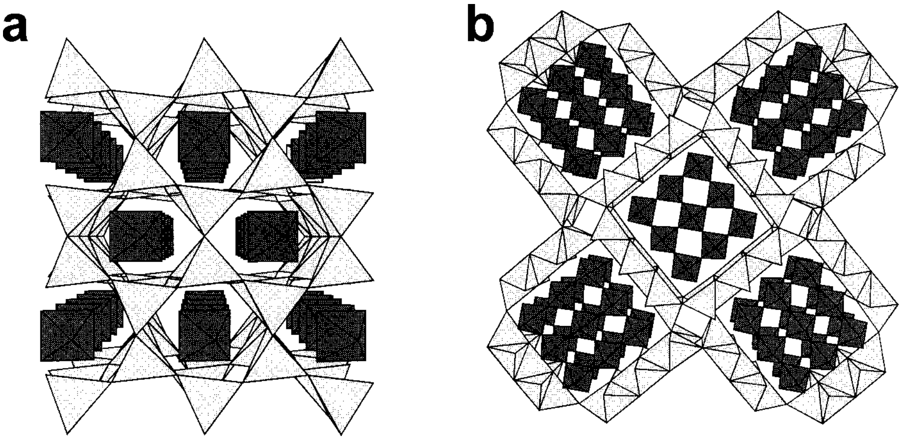
CCP units as "guest molecules" in ACT units. ACT layers and frameworks usually have large holes or channels that are occupied either by CCP finite units and chains, or interstitial ions. Figure 3a shows an oxocentered tetrahedral layer formed by continuous linking of (OA_4) tetrahedra via edges. Litharge, PbO, consists solely of such a layer of (OPb_4) tetrahedra. This layer was observed also in several oxychloride minerals, e.g., in asisite, Pb_8O_7Cl (Rouse et al. 1988). Figure 3b

TABLE 3. Structural systematics of minerals and inorganic compounds containing anion-centered tetrahedral units and cation-centered polyhedral units of different dimensionality

	D_{CCPU}			
D_{ACTU}	0	1	2	3
0	fedotovite $K_2[Cu_3O](SO_4)_3$,	$[Pb_3O][UO_5]$		$(Pb^{4+})_{14}(Pb^{2+})_{18}(Pb_4O_4)_8Si_{100}Al_{92}O_{384}$
0	euchlorine $NaK[Cu_3O](SO_4)_3$, $(Cu_4O)(PO_4)_2$			maricopaite $Pb_7Ca_2Al_{12}Si_{36}(O,OH)_{100}\cdot m(H_2O,OH)$
0	$[Sn_2O](SO_4)$, $(Ca_4O)(PO_4)_2$			$[Zn_4O][BO_2]_6$
0	$[Sr_2Bi_3O_2](VO_4)_3$			
1	kamchatkite $K[Cu_3O](SO_4)_2Cl$	$[PbGeO][Ge_2O_6]$	$Pb[Pb_2MnAl_2O_4][Al_8O_{18}]$	
1	chloromenite $Cu_3[Cu_6O_2](SeO_3)_4Cl_6$	chloroxiphite $[Pb_3O_2][Cu(OH)_2]Cl_2$		
1	stoiberite $[Cu_5O_2](VO_4)_2$			
1	georgbokiite $[Cu_5O_2](SeO_3)_2Cl_2$			
1	lanarkite $[Pb_2O](SO_4)$			
1	$[Yb_2O](SiO_4)$			
1	freedite $[Pb_8O_3]Cu(AsO_3)_2Cl_5$			
1	$[Pb_2O](SiO_3)$			
2	averievite $[Cu_5O_2](VO_4)_2\cdot MCl$		$[NdO][ZnAs]$, $[NdO][ZnP]$	
2	ilinskite $Na[Cu_5O_2](SeO_3)_2Cl_3$			
2	dolerophanite $[Cu_2O](SO_4)$			
2	francisite $[Cu_3BiO_2](SeO_3)_2Cl$			
2	kombatite $[Pb_{14}O_9](VO_4)_2Cl_4$			
2	$[Gd_2O](SiO_4)$			
2	$[Pb_5O_3](GeO_4)$			
2	bismuthite $[Bi_2O_2](CO_3)$			
3	$[Cu_2O](SeO_3)$-I,II	$[Pb_{12}O_{12}][Ta_9O_8F_{29}]$		$[La_3O_2][Ir_3O_9]$
3	$[Cu_5SnO_4](BO_3)_2$			$[LuPb_2O_2][Al_3O_6]$
3	$[Hg_3O_2](CrO_4)$			



→ **FIGURE 3.** The adaptation of ACT layers (light) to cation-centered tetrahedra (dark) (see



← **FIGURE 4.** Chains of cation-centered octahedra (dark) in the channels of ACT frameworks (light) (see text).

shows the layer $^{2}_{\infty}[O_9Pb_{14}]$ from kombatite, $Pb_{14}O_9(VO_4)_2Cl_4$ (Cooper and Hawthorne 1994), which may be obtained by replacing blocks of seven (OPb_4) tetrahedra by two (VO_4) tetrahedra. In $Pb_5O_3(GeO_4)$ (Kato 1979), six oxocentered tetrahedra are replaced by two (GeO_4) groups (Fig. 3c). Other examples of high-dimensional ACT units with CCP guests are shown in Figure 4. The structures of the rare earth niobates with general formula $[A_3O_2][NbO_5]$ (Klimenko et al. 1992; Vente et al. 1994) consist of $^{3}_{\infty}[O_2A_3]$ oxocentered tetrahedral frameworks with large hexagonal channels occupied by single chains of corner-sharing (NbO_6) octahedra (Fig. 4a). Sixfold corner-sharing chains of (TaX_6) octahedra (X = O, F) occupy large square channels in $^{3}_{\infty}[XPb]$ ACT framework built by cross-condensation of chains of (XPb_4) tetrahedra (X = O, F) in $Pb_{12}Ta_9O_{20}F_{29}$ (Sävborg 1985a) (Fig. 4b). The shape of these ACT units may be dictated by the presence of cation-centered octahedra that need suitable channels.

Whereas the "face-to-face" principle works in structures with small anion-centered tetrahedra, the second principle of "guest molecules" is more appropriate for ACT units built from large tetrahedra.

$D_{\text{CCPU}} > D_{\text{ACTU}}$

$\boldsymbol{D_{\text{CCPU}} = 2}$**.** Figure 5 shows two examples of structures consisting of CCP layers and ACT chains. The structure of $Pb_3Ta_5O_9F_{13}$ (Sävborg 1985b) based on the $^{2}_{\infty}[Ta_5X_{19}]$ layers built from corner-sharing (TaX_6) octahedra (X = O, F) and $^{1}_{\infty}[FPb_3]$ single chains of corner-sharing (FPb_4) tetrahedra (Fig. 5a). The structure of $Pb[Pb_2MnAl_2O_2][Al_8O_{18}]$ (Teichert and Müller-Buschbaum 1991) contains $^{2}_{\infty}[Al_4O_9]$ aluminate tetrahedral layers and $^{1}_{\infty}[O_2Pb_2MnAl_2]$ oxocentered tetrahedral chains (Fig. 5b). In both cases, the flexible CCP layers form appropriate hollows to accommodate large ACT chains.

$\boldsymbol{D_{\text{CCPU}} = 3}$**.** In this case, the ACT units occur in cavities of the cation-centered polyhedral frameworks. This is clearly the reverse situation to that described in the previous section. Here, large anion-centered polycations can be considered as guest molecules that control the type of CCP framework, as illustrated by maricopaite (Rouse and Peacor 1994). Maricopaite is a zeolite-like mineral with an unusual mordenite-like interrupted tetrahedral framework (Fig. 6). Its cavities contain large polycations $[Pb_4(OH)_4]^{4+}$ that may be described as Pb_4 tetrahedra with O atoms capping all their faces. The O atoms have tetrahedral coordination, consisting of three O-Pb and one O-H bonds. Rouse and Peacor (1994) suggested that maricopaite crystallized around the $[Pb_4(OH)_4]$ complexes that are already existed in the formative solutions and that the framework discontinuities result from the necessity to accommodate these large structural units. Such anion-centered clusters may be introduced into the framework cavities after it has formed. An example is the structure of Pb^{2+}-exchanged and dehydrated zeolite X, the synthetic counterpart of faujasite (Yeom et al. 1997);

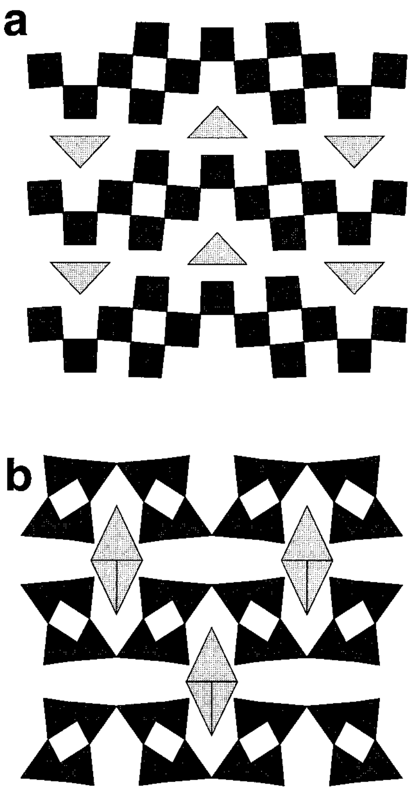


FIGURE 5. Accommodation of CCP layers (dark) to ACT chains (light) (see text).

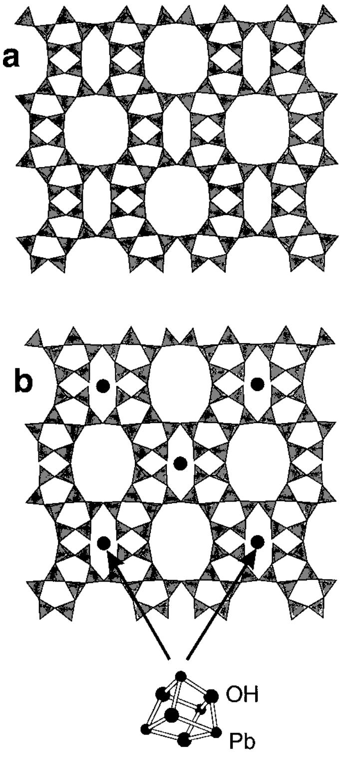


FIGURE 6. Undistorted (**a**) and interrupted (**b**) tetrahedral frameworks in mordenite and maricopaite, respectively. Framework discontinuities in maricopaite result from the necessity to accommodate $[Pb_4(OH)_4]$ clusters (**b**).

the $[Pb_4(OH)_4]$ complexes are exchangeable polycations that balance the negative charge of the framework. Dehydration of these complexes leads to the formation of $[Pb_8O_4]$ polycations by replacing H by Pb. These complexes have a geometry of stella quandrangula, a common metal-cluster arrangement in complex-alloy structures (Nyman and Andersson 1979; Andersson 1981; Häussermann et al. 1998).

$D_{CCPU} = D_{ACTU} > 1$

The main principles for constructing crystal structures containing ACT and CCP units with the same dimensionality are parallel juxtaposition for $D = 1, 2$ and interpenetration for $D = 3$.

$D = 1, 2$. This case is illustrated by the structure of chloroxiphite, $[Pb_3O_2][Cu(OH)_2]Cl_2$ (Finney et al. 1977), which is based on the double $^{1}.[O_2Pb_3]$ chains of edge-sharing (OPb_4) tetrahedra (like that shown in Fig. 1a) and $^{1}.[Cu(OH)_2]$ column s of edge-sharing $[Cu(OH)_4]$ squares extending parallel to the **b** axis. The structure of compounds with alternating anion- and cation-centered tetrahedral layers were described recently by Nientiedt and Jeitschko (1998).

$D = 3$. When the anion- and cation-centered polyhedral units are three-dimensional, they interpenetrate in the structure (Fig. 7). The anion-centered tetrahedral unit is built by corner sharing of stellae quadrangulae, $[O_4A_8]$. This type of interpenetration between ACT and CCP units occurs in $[Bi_3O_2][Ru_3O_9]$ (Abraham and Thomas 1975; see also: Sleight and Bouchard 1973). The interpenetration of ACT- and CCP-three-dimensional units implies that each framework has large cavities for location of fundamental blocks of another unit.

STRUCTURES WITHOUT CCP UNITS

The general crystal-chemical formula of minerals and compounds with ACT but without CCP units may be written as $A'_k[X_nA_m]X'_l$, where A' represents a cation that does not belong to anion-centered tetrahedra, and X' is a large anion (usually halide or S^{2-}). These structures are controlled by adjustment between ACT units and large anions. Two structural groups may be distinguished by the dimensionality of their tetrahedral units: $D < 3$ (finite groups, chains and layers) and $D = 3$ (frameworks). When A' and X' are missing, we have simple $[X_nA_m]$ compounds,

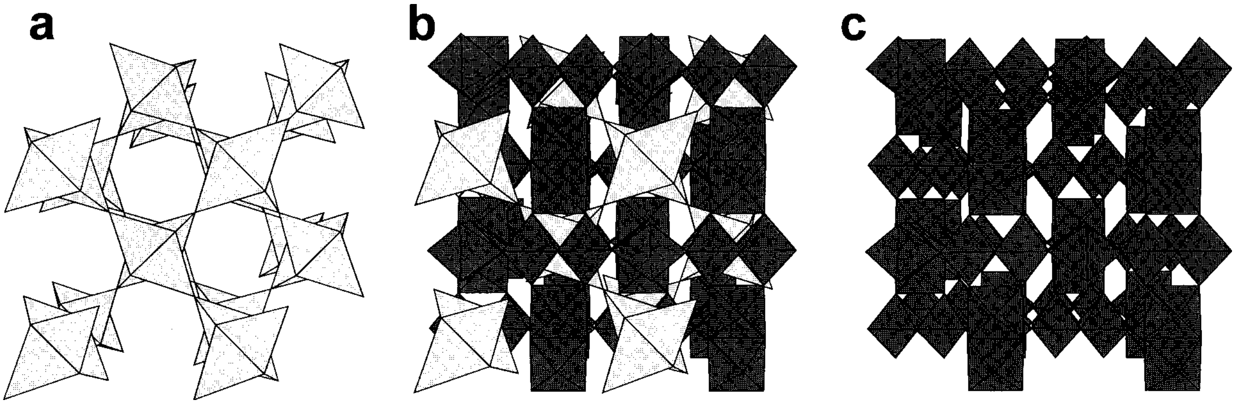


FIGURE 7. The scheme of interpenetration between anion-centered tetrahedral $^{3}_{\infty}[O_2Bi_3]$ (**a**) and cation-centered $^{3}_{\infty}[Ru_3O_9]$ octahedral (**c**) frameworks in $[Bi_3O_2][Ru_3O_9]$ (**b**).

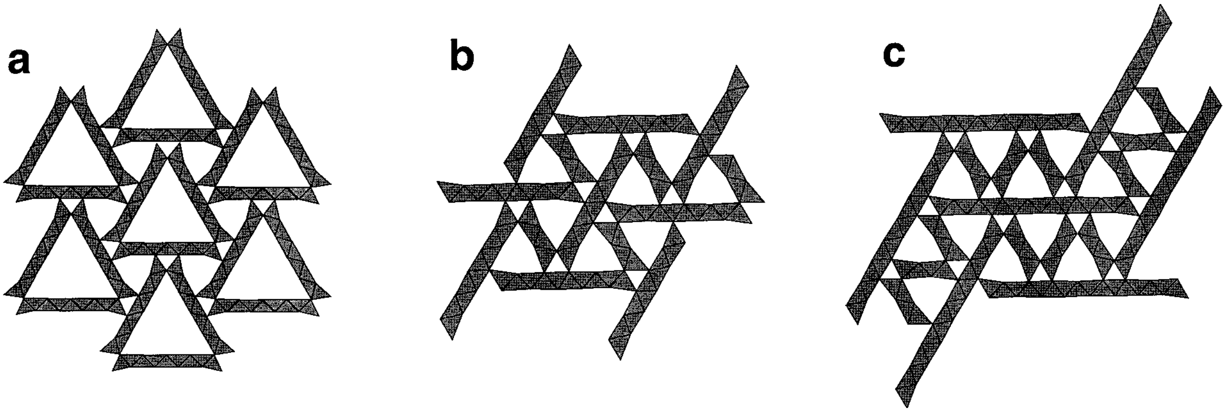


FIGURE 8. Oxocentered tetrahedral frameworks built by condensation of (OBi_4) tetrahedra: (**a**) $^{3}_{\infty}[O_9Bi_8]$ framework from $(Cu_5Cl)Bi_{48}O_{59}Cl_{30}$ (Aurivillius 1990) built from ninefold chains; (**b**) $^{3}_{\infty}[(O_6F)Bi_6]$ framework from $Bi_6O_7FCl_3$ (Hopfgarten 1975) built from tenfold and fourfold chains; (**c**) $^{3}_{\infty}[O_7Bi_6]$ framework from $Bi_{12}O_{15}Cl_6$ (Hopfgarten 1976) built from 16-fold and fourfold chains.

such as oxides and fluorides considered by O'Keeffe and Hyde (1985, 1996) and Hyde and Andersson (1989).

Structures with ACT finite groups, chains, and layers.

The main function of large anions in structures of this type is to surround tetrahedral units and/or to link them into the complex units incorporating tetrahedra as a core. The structure of ponomarevite, $K_4Cu_4OCl_{10}$ (Semenova et al. 1989) consists of $[(OCu_4)Cl_{10}]^{4-}$ clusters which represent (OCu_4) oxocentered tetrahedra surrounded by ten chlorine ions. Potassium ions, K^+, unite these clusters into a three-dimensional structure. In the structure of mendipite, $Pb_3O_2Cl_2$ (Gabrielson 1958), double ${}^1_\infty[O_2Pb_3]$ chains like that shown in Figure 1a are linked by chlorine atoms into a framework. Thorikosite, $(Pb_3Sb_{0.6}As_{0.4})(O_3OH)Cl_2$ (Rouse and Dunn 1985), consists of Cl anions sandwiched between litharge-like layers of oxocentered tetrahedra (Fig. 3a).

Structures with ACT frameworks

Large X' anions fill the cavities of anion-centered tetrahedral frameworks (Fig. 8). These frameworks have large one-dimensional channels suitable for the occurence of large anions.

Conformation of single chains of edge sharing (XA_4) tetrahedra

In some structures containing ${}^1_\infty[XA_2]$ chains of edge-sharing (XA_4) tetrahedra and large halide ions (X'), tetrahedral chains accommodate large anions by rotation of anion-centered tetrahedra about axes normal to the extension of the chain. Rotation of this kind is reminiscent of that observed in corner-sharing (SiO_4) tetrahedra in silicates (Liebau 1985). The effect of such a rotation is to transform the zweier single chain (i.e., having two tetrahedra within the identity period) toward the vierer chain (with four tetrahedra in the identity period) and has been observed, for example, in coparsite, $[Cu_4O_2][(As,V)O_4]Cl$ (Starova et al. 1998). The detailed description of the conformation of ${}^1_\infty[XA_2]$ chains in the presence of large halide ions is given by Krivovichev and Filatov (1998).

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