

REFINEMENT OF THE CRYSTAL STRUCTURE OF BLOEDITE: STRUCTURAL SIMILARITIES IN THE $[^VI M(^IV T\Phi_4)_2\Phi_n]$ FINITE-CLUSTER MINERALS

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ABSTRACT

The crystal structure of bloedite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, monoclinic, a 11.126(2), b 8.242(1), c 5.539(1) Å, β 100.84(1)°, V 498.8(1) Å³, $Z = 2$, space group $P2_1/a$, has been refined to a residual R of 3.1% on 1304 observed (4σ) reflections of graphite-monochromated $\text{MoK}\alpha$ radiation. Hydrogen atoms were located, and a sensible hydrogen-bond arrangement shows up in the refined structure. The fundamental building block (FBB) of the structure is the $[\text{Mg}(\text{H}_2\text{O})_4(\text{SO}_4)_2]^{2-}$ finite heteropolyhedral cluster, which is repeated by translations to form rather open sheets// (001) ; these sheets are linked together by octahedrally co-ordinated sodium and hydrogen bonding. The $[^VI M(^IV T\Phi_4)_2\Phi_4]$ cluster is the FBB of the bloedite, leonite, anapaite and schertelite structures, and the open sheets of these clusters form a structure module that is also common to all four types of structure.

Keywords: crystal structure, sulfate, mineral, bloedite.

SOMMAIRE

La structure cristalline de la bloedite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, monoclinique, a 11.126(2), b 8.242(1), c 5.539(1) Å, β 100.84(1)°, V 498.8(1) Å³, $Z = 2$, groupe spatial $P2_1/a$, a été affinée jusqu'à un résidu R de 3.1% sur 1304 réflexions observées en radiation $\text{MoK}\alpha$ monochromatisée sur graphite. On a localisé les atomes d'hydrogène, et une disposition satisfaisante de liaisons hydrogène apparaît dans la structure affinée. L'élément fondamental ou "bloc de construction" (FBB) de la structure est le groupement hétéropolyédrique $[\text{Mg}(\text{H}_2\text{O})_4(\text{SO}_4)_2]^{2-}$, qui se répète par translations pour former des feuillets assez ouverts parallèlement à (001) ; ces feuillets se relient entre eux par le sodium en coordination octaédrique et par liaisons hydrogène. Le groupement $[^VI M(^IV T\Phi_4)_2\Phi_4]$ est le FBB commun aux structures cristallines de bloedite, leonite, anapaite et schertelite, et les feuillets ouverts de ces groupements constituent un module structurel commun, lui aussi, aux quatre types de structure.

(Traduit par la Rédaction)

Mots-clés: structure cristalline, sulfate, minéral, bloedite.

INTRODUCTION

Bloedite is a hydrated sodium magnesium sulfate mineral that is a common phase in salt deposits of marine and lacustrine origin. It has a wide field of stability at 25°C in the reciprocal salt system Na-Mg-Cl-SO_4 (Eugster & Hardie 1980), and precipi-

tates directly as a result of evaporative concentration from saline waters. The structure of bloedite was solved by Rumanova (1958), and the structure of the zinc analogue was reported by Giglio (1958). A neutron structure-refinement of the cobalt analogue was given by Bukin & Nozik (1975).

In a recent examination of the $^VI M(^IV T_2\Phi_n)$ (unspecified ligand) minerals (Hawthorne 1985), bloedite was one of a number of minerals whose structure was shown to be based on finite *trans* $M(T\Phi_4)_2\Phi_4$ clusters. A more detailed examination of these structures was thought desirable, together with more accurate information on the structure of bloedite itself, and thus the current study was undertaken.

EXPERIMENTAL

The material used in this study is from Soda Lake, San Luis Obispo County, California, and was obtained from the Department of Mineralogy and Geology, Royal Ontario Museum, collection number M35298. A crystal was mounted on a Nicolet R3m automated four-circle diffractometer equipped with a molybdenum-target X-ray tube and a crystal monochromator of highly oriented graphite mounted with equatorial geometry. Twenty-five reflections were centred, and least-squares refinement of the setting angles produced the monoclinically constrained cell-dimensions given in Table 1, together with the orientation matrix relating the crystal axes to the diffractometer axes.

Intensity data were collected in the θ - 2θ scan mode, using 96 steps with a scan range from $[2\theta(\text{MoK}\alpha_1) - 1]$ to $[2\theta(\text{MoK}\alpha_2) + 1]$ ° and a variable scan-rate between 4.0 and 29.3°/minute depending on the intensity of an initial 1 s count at the centre of the scan range. Backgrounds were measured for half the scan time at the beginning and end of each scan. Two standard reflections were monitored every 48 measurements to check for stability and constancy of crystal alignment. A total of 1461 reflections were measured over one asymmetric unit out to a maximum 2θ of 60°. Ten strong reflections uniformly distributed with regard to 2θ were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0 to 350°. These data were used to calculate an ellipsoidal empirical absorption-correction, the

TABLE 1. MISCELLANEOUS INFORMATION: BLOEDITE

a	11.126(2) \AA	Crystal Size (mm)	0.16x0.22x0.35
b	8.242(1)	Rad/Mono	MoK α /Graphite
c	5.539(1)	Total Fo	1461
β	100.84(1) $^\circ$	Fo > 4 σ	1304
V	498.8(1) \AA^3	Final R(obs)	3.1%
Space Group	P2 $_1$ /a	Final R $_w$ (obs)	3.4%
Unit cell contents: 2[Na $_2$ Mg(SO $_4$) $_2$ (H $_2$ O) $_4$]			
$R = \Sigma(Fo - Fc) / \Sigma Fo $			
$wR = [\Sigma w(Fo - Fc)^2 / \Sigma wFo^2]^{1/2}$, $w=1$			

R (symmetric) index being reduced from 10.0% to 2.2% for the azimuthal data. This correction was then applied to the whole data-set, minimum and maximum transmission being 0.374 and 0.728, respectively. The data were also corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors; of the 1461 unique reflections, 1304 were classed as observed ($>4\sigma$).

STRUCTURE REFINEMENT

Scattering curves for neutral atoms, together with coefficients of anomalous dispersion, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). R indices are of the form given in Table 1 and are expressed as percentages. The SHELXTL (Sheldrick 1981) system of programs was used for the computational aspects of this work.

Using the structural parameters given by Giglio (1958) for synthetic Na $_2$ Zn(SO $_4$) \cdot 4H $_2$ O, least-squares refinement of all positional parameters for an isotropic thermal model converged to an R index of 4.1%. At the time of the refinement, I was not aware of the neutron study of Bukin & Nozik (1975). Consequently the H positions were not taken from the neutron study, but were directly determined in this work.

A difference-Fourier map calculated at this stage clearly revealed all hydrogen atoms. Insertion of these positions into the least-squares refinement (with fixed isotropic temperature-factors) together with conversion of non-hydrogen-atom temperature-factors to the anisotropic form resulted in convergence at an R index of 3.1%. Final positional parameters are given in Table 2, and anisotropic temperature-factor coefficients are given in Table 3. Selected interatomic distances are listed in Table 4 and a bond-valence analysis is given in Table 5. Observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION

Description of the bloedite structure

The structure reported by previous authors is confirmed. Sulfur is surrounded by an irregular tetrahedral array of oxygen atoms; deviations from ideal tetrahedral geometry are not large, and the small variations in individual S-O bond lengths may be interpreted in terms of local bond-valence requirements. Magnesium is co-ordinated by two oxygen atoms and four (H $_2$ O) groups, arranged in a slightly distorted octahedral array; the observed $\langle \text{Mg-O} \rangle$ distance of 2.076 \AA agrees closely with the sum of the ionic radii (Shannon 1976). Sodium is co-ordinated by four oxygen atoms and two (H $_2$ O) groups, arranged in a very distorted octahedral configuration. The O-Na-O bond angles deviate by up to $\sim 25^\circ$ from the

TABLE 2. POSITIONAL PARAMETERS FOR BLOEDITE

Site	x	y	z	$U_{\text{equiv.}}^+$
S	0.13640(4)	0.29075(6)	0.36935(8)	1.05(1)
Mg	0	0	0	1.07(1)
Na	0.36178(8)	0.0705(1)	0.1305(2)	2.01(3)
O(1)	0.2663(1)	0.2712(2)	0.3476(3)	1.96(4)
O(2)	0.0802(1)	0.4214(2)	0.2091(3)	2.03(5)
O(3)	0.0704(2)	0.1372(2)	0.3058(3)	1.90(4)
O(4)	0.1321(2)	0.3283(2)	0.6297(3)	1.96(5)
O(5)	0.1603(1)	0.0378(2)	0.8727(3)	1.47(4)
O(6)	0.0809(2)	0.7908(2)	0.1774(3)	1.73(4)
H(5)A	0.153(2)	0.119(3)	0.802(5)	1.0*
H(5)B	-0.175(2)	0.034(3)	0.215(5)	1.0
H(6)A	0.466(2)	0.226(3)	0.755(5)	1.0
H(6)B	-0.137(3)	0.202(3)	-0.276(5)	1.0

* fixed; $^+ U_{\text{equiv.}} = U_{\text{equiv.}} \times 10^2$

TABLE 3. ANISOTROPIC TEMPERATURE-FACTOR COEFFICIENTS FOR BLOEDITE

Atom	U_{11}^*	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	108(2)	107(2)	96(2)	-9(2)	11(1)	4(2)
Mg	106(4)	100(4)	114(4)	-13(3)	21(3)	-5(3)
Na	177(4)	196(4)	221(4)	15(3)	18(3)	-8(4)
O(1)	114(6)	214(8)	263(8)	15(6)	47(6)	21(7)
O(2)	173(7)	200(8)	225(8)	41(6)	14(6)	106(6)
O(3)	243(8)	172(7)	148(7)	-104(6)	23(6)	-40(6)
O(4)	312(9)	165(7)	116(6)	-35(6)	52(6)	-42(6)
O(5)	158(7)	142(7)	154(7)	4(6)	61(6)	7(6)
O(6)	161(7)	149(7)	179(7)	-15(6)	-43(6)	29(6)

* $U_{ij} = U_{ij} \times 10^4$

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN BLOEDITE

S-O(1)	1.481(2)	Na-O(1)	2.407(2)
S-O(2)	1.459(2)	Na-O(2)f	2.433(2)
S-O(3)	1.472(2)	Na-O(2)g	2.388(2)
S-O(4)	1.484(2)	Na-O(4)h	2.391(2)
<S-O>	1.474	Na-O(5)b	2.436(2)
		Na-O(6)f	2.650(2)
		<Na-O>	2.451
Mg-O(3),a	2.065(2) x2		
Mg-O(5)b,c	2.061(2) x2		
Mg-O(6)d,e	2.101(2) x2		
<Mg-O>	2.076		
O(1)-O(2)	2.410(2)	O(1)-S-O(2)	110.1(1)
O(1)-O(3)	2.415(2)	O(1)-S-O(3)	109.7(1)
O(1)-O(4)	2.402(2)	O(1)-S-O(4)	108.2(1)
O(2)-O(3)	2.410(2)	O(2)-S-O(3)	110.6(1)
O(2)-O(4)	2.417(2)	O(2)-S-O(4)	110.4(1)
O(3)-O(4)	2.389(2)	O(3)-S-O(4)	107.8(1)
<O-O>S	2.407	<O-S-O>	109.5
O(3)-O(5)b	2.887(2)	O(3)-Mg-O(5)b	88.8(2) x2
O(3)-O(5)c	2.948(2)	O(3)-Mg-O(5)c	91.2(1) x2
O(3)-O(6)d	2.951(2)	O(3)-Mg-O(6)d	90.2(1) x2
O(3)-O(6)e	2.941(2)	O(3)-Mg-O(6)e	89.8(1) x2
O(5)b-O(6)d	2.886(3)	O(5)b-Mg-O(6)d	87.8(1) x2
O(5)b-O(6)e	2.999(3)	O(5)b-Mg-O(6)e	92.2(1) x2
<O-O>Mg	2.935	<O-Mg-O>	90.0
O(1)-O(2)g	4.040(4)	O(1)-Na-O(2)g	114.8(1)
O(1)-O(4)h	3.817(3)	O(1)-Na-O(4)h	105.4(1)
O(1)-O(5)b	3.294(3)	O(1)-Na-O(5)b	85.7(1)
O(1)-O(6)f	3.639(3)	O(1)-Na-O(6)f	91.9(1)
O(2)f-O(2)g	2.957(2)	O(2)f-Na-O(2)g	75.3(1)
O(2)f-O(4)h	3.453(3)	O(2)f-Na-O(4)h	91.4(1)
O(2)f-O(5)b	3.156(3)	O(2)f-Na-O(5)b	80.8(1)
O(2)f-O(6)f	3.050(3)	O(2)f-Na-O(6)f	73.6(1)
O(2)g-O(4)h	3.379(3)	O(2)g-Na-O(4)h	90.0(1)
O(2)g-O(6)f	3.067(3)	O(2)g-Na-O(6)f	74.8(1)
O(4)i-O(5)b	3.676(3)	O(4)i-Na-O(5)b	99.2(1)
O(5)b-O(6)f	3.609(3)	O(5)b-Na-O(6)f	90.3(1)
<O-O>Na	3.428	<O-Na-O>	89.4
O(5)-H(5)A	0.77(3)	H(5)A-O(4)	1.96(3)
O(5)-H(5)B	0.81(3)	H(5)B-O(1)	1.93(3)
H(5)A-H(5)B	1.30(4)	H(5)A-O(5)-H(5)B	110(3)
O(5)-O(4)	2.736(2)	O(5)-H(5)A-O(4)	178(3)
O(5)-O(1)j	2.713(2)	O(5)-H(5)B-O(1)j	165(3)
O(6)-H(6)A	0.88(3)	H(6)A-O(4)g	2.14(3)
O(6)-H(6)B	0.75(3)	H(6)B-O(1)j	2.17(3)
H(6)A-H(6)B	1.27(4)	H(6)A-O(6)-H(6)B	103(3)
O(6)-O(4)g	2.945(3)	O(6)-H(6)A-O(4)g	152(2)
O(6)-O(1)j	2.857(3)	O(6)-H(6)B-O(1)j	152(3)

a: \bar{x}, y, z ; b: $x, y, z-1$; c: $\bar{x}, y, 1-z$; d: $x, y-1, z$; e: $\bar{x}, 1-y, z$; f: $1/2-x, y-1/2, z$; g: $1/2+x, 1/2-y, z$; h: $1/2-x, y-1/2, 1-z$; i: $x-1/2, 1/2-y, z$; j: $x-1/2, 1/2-y, z-1$.

(H₂O) groups are slightly shorter than their ideal values. However, the local geometry is compatible with the range of values found by neutron diffraction in many hydrates (Baur 1972, Ferraris & Franchini-Angela 1972), and shows good agreement with the neutron-diffraction results of Bukin & Nøzik (1975) on the synthetic cobalt analogue. The arrangement leads to a sensible distribution of hydrogen bonds (Table 4, Fig. 1). Both O(5) and O(6) are hydrogen-bond donors to O(1) and O(4); as shown in Table 5, the hydrogen bonds have a major role in the satisfaction of local bond-valence requirements for O(1) and O(4), both of which have bond-valence sums of ~ 1.6 v.u. when hydrogen bonding is not considered.

The overall structural arrangement of bloedite is shown in Figure 2. The fundamental building block (FBB) of the structure is the $[\text{Mg}(\text{H}_2\text{O})_4(\text{SO}_4)_2]^{2-}$ finite heteropolyhedral cluster, shown shaded in Figure 2. These are repeated by the translational symmetry operations of the structure to form rather open sheets parallel to (001); these are linked together by octahedrally co-ordinated Na and inter-FBB hydrogen bonding.

The $[\text{VI}M(\text{IV}T\Phi_4)_2\Phi_n]$ finite-cluster structures

Hawthorne (1985) has shown that the structures of several minerals are based on finite heteropolyhedral clusters of the form $[\text{VI}M(\text{IV}T\Phi_4)_2\Phi_n]_m$. The *trans* $[\text{M}(T\Phi_4)_2\Phi_4]$ cluster is the most common, being the fundamental building block (FBB) of the

TABLE 5. EMPIRICAL BOND-VALENCE* TABLE FOR BLOEDITE

	S	Mg	Na	H(5)A	H(5)B	H(6)A	H(6)B	Σ
O(1)	1.477		0.184		0.2		0.2	2.061
O(2)	1.575		0.176					1.941
O(3)	1.516	0.355 $\frac{x^2}{2}$	0.190					1.871
O(4)	1.464		0.189	0.2		0.2		2.053
O(5)		0.358 $\frac{x^2}{2}$	0.175	0.8	0.8			2.133
O(6)		0.330 $\frac{x^2}{2}$	0.122			0.8	0.8	2.052
Σ	6.032	2.086	1.036	1.0	1.0	1.0	1.0	

*calculated from the curves of Brown (1981), bond-valences in valence units (v.u.).

ideal value of 90°; it is notable that the mean value of the O-Na-O bond angles differs from 90°, a characteristic of highly distorted octahedral coordination polyhedra. The O-H bond lengths in the

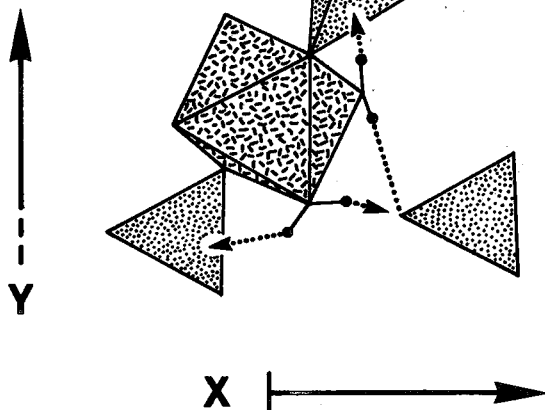


FIG. 1. The hydrogen-bond arrangement in bloedite; octahedra are dashed, tetrahedra are dotted. Hydrogen bonds with arrows indicate bonding to an anion one unit-cell translation away from the anion shown in the figure.

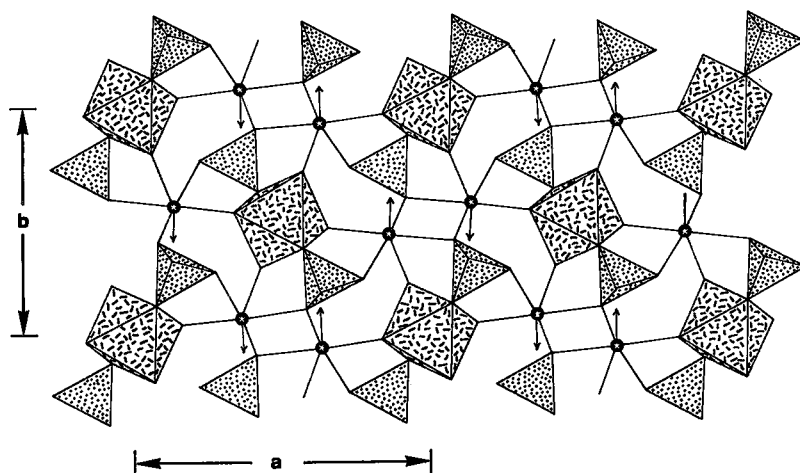


FIG. 2. The structure of bloedite projected on (001); Na is represented by the starred circles, rest of legend as in Figure 1.

TABLE 6. MINERALS BASED ON FINITE HETEROPOLYHEDRAL CLUSTERS OF THE FORM $[^{VI}M(^{IV}T\Phi_4)_2\Phi_n]$

Mineral	Formula	a(Å)	b(Å)	c(Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	Sp.Gr.	Ref.
Bloedite	$\text{Na}_2[\text{Mg}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$	11.126(2)	8.242(1)	5.539(1)	-	100.84(1)	-	P2 ₁ /a	(1)
Leonite-(Mn)	$\text{K}_2[\text{Mn}^{2+}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$	12.03(3)	9.61(3)	9.98(4)	-	95.0(3)	-	C2/m	(2)
Anapaite	$\text{Ca}_2[\text{Fe}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_4]$	6.447(1)	6.816(1)	5.898(1)	101.64(3)	104.24(3)	70.76(4)	P $\bar{1}$	(3)
Schertelite	$(\text{NH}_4)_2[\text{Mg}(\text{PO}_3\text{OH})_2(\text{H}_2\text{O})_4]$	11.49(2)	23.66(6)	8.62(1)	-	-	-	Pbca	(4)

References: (1) this study; (2) Srikanta et al. (1988); (3) Catti et al. (1979); (4) Khan & Baur (1972)

bloedite, leonite, schertelite and anapaite structures (Table 6). Despite the differences in chemistry and symmetry between these minerals, the clusters have a very similar arrangement in each structure. The clusters are arranged in open sheets, as shown in Figure 3, and bonding within and between the sheets involves both hydrogen bonding and linkage through large low-valence cations. Although the geometrical details of the cluster vary from structure to structure, the basic array of clusters within the sheets is the same. They are arranged in a centred rectangular array with the projection of the long axis of the cluster parallel to one of the crystallographic axes. The bloedite sheet (Fig. 2) is different from the others (Fig. 3) in that the nearest-neighbor clusters are canted in opposite directions.

The stacking of these open sheets is illustrated in Figure 4. Again it can be seen that adjacent clusters are canted in opposite directions in bloedite, and in the same direction in anapaite, leonite, and schertelite. The large low-valence cations are in layers parallel to the open sheets of clusters, and are the principal agent holding the sheets together.

Hence not only do these minerals have the (graphically) same type of fundamental building block, the $[^{VI}M(^{IV}T\Phi_4)_2\Phi_n]$ heteropolyhedral cluster, but they also have the same type of structure module (Hawthorne 1985), the $[^{VI}M(^{IV}T\Phi_4)_2\Phi_n]_{\infty}$ open sheet. The geometrical details of the sheets vary from structure to structure, presumably in response to the varying bond-valence requirements of the linking low-valence cations. Each different large low-valence cation has slightly different bonding requirements, and these open sheets are sufficiently flexible to adjust to these requirements and still maintain their general arrangement.

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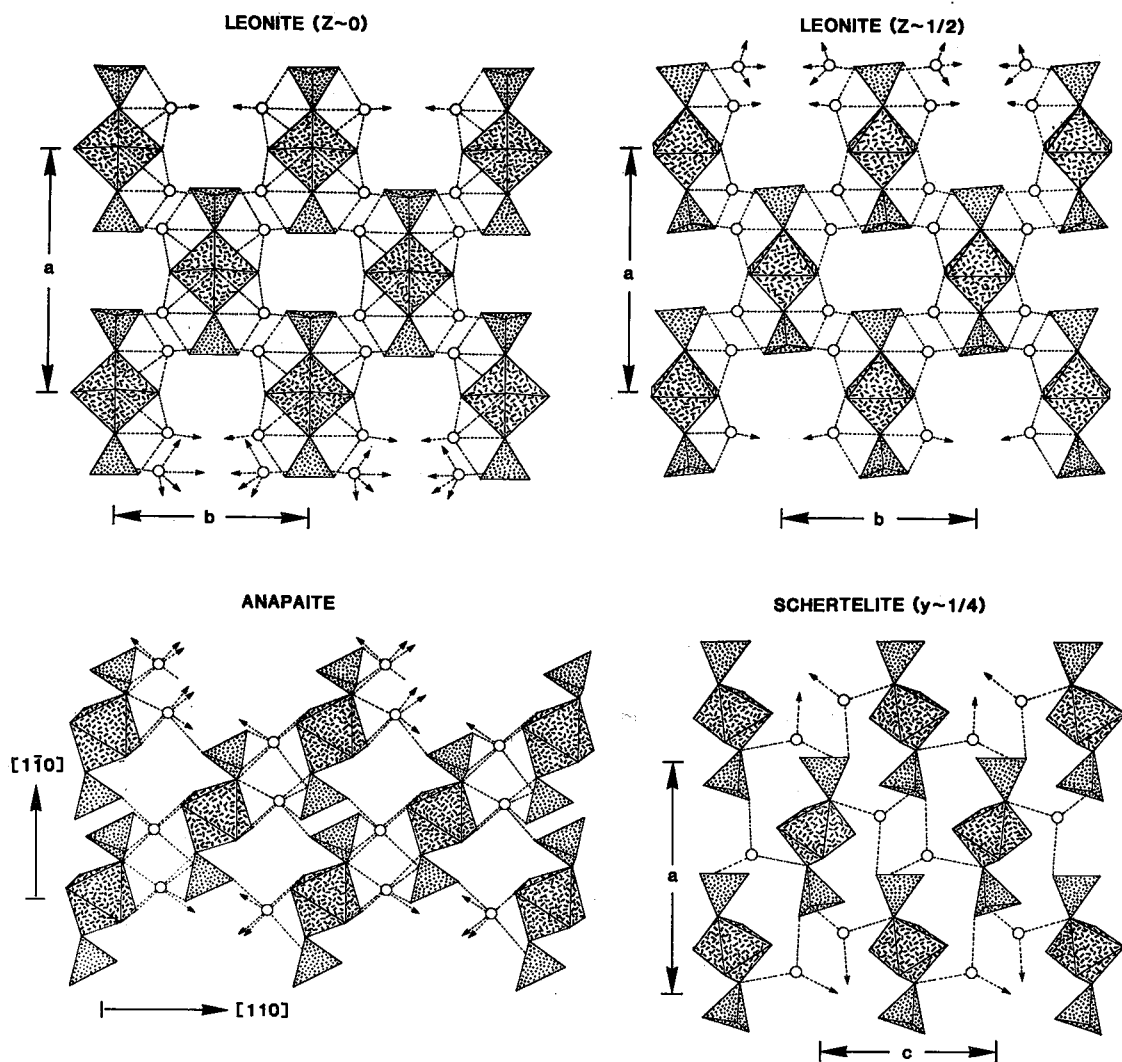


FIG. 3. The open sheets of $trans [M(T\Phi_4)_2\Phi_4]$ clusters that are found in the structures of leonite, anapaite and schertelite; compare also with Figure 2.

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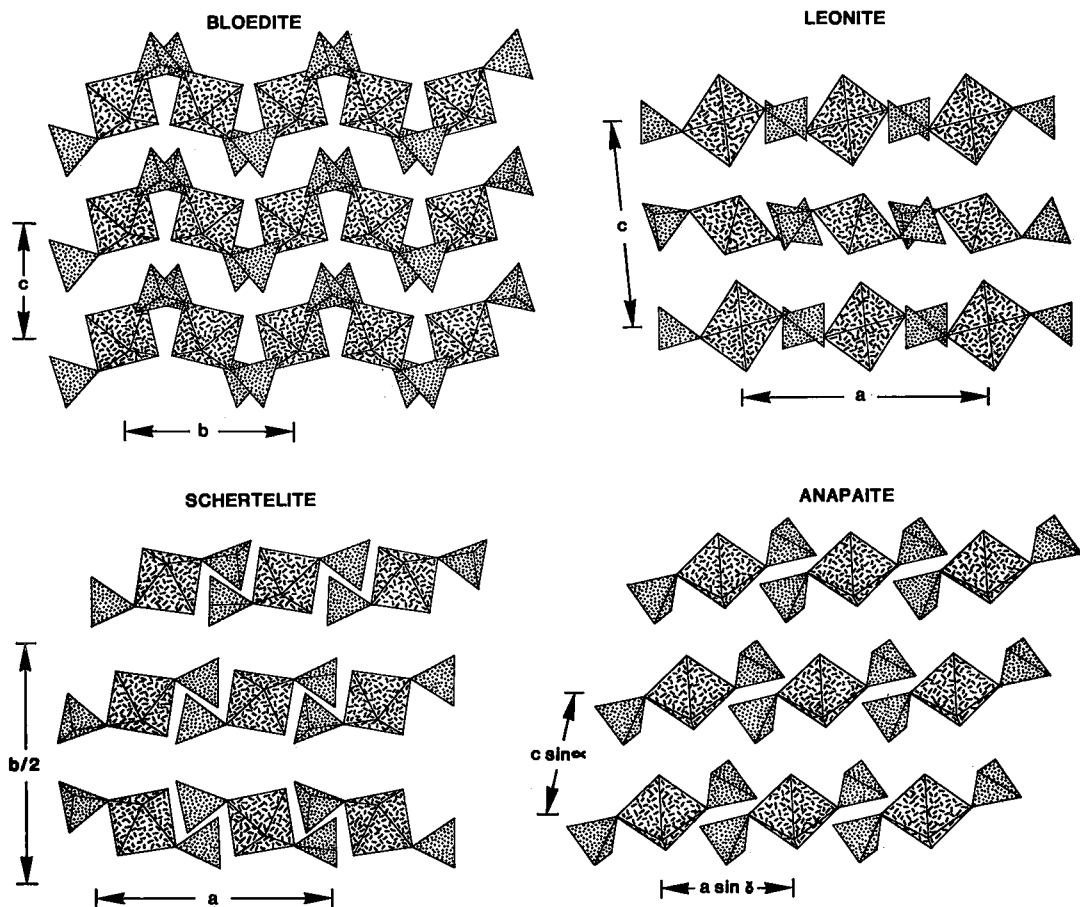


FIG. 4. The $[M(T\Phi_4)_2\Phi_4]$ finite-cluster structures, showing the layered nature of the structures produced by stacking of the open sheets shown in Figures 2 and 3.

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