Russian Chemical Reviews **67** (2) 137 – 155 (1998) © 1998 Russian Academy of Sciences and Turpion Ltd

UDC 548.736

Types of cationic complexes based on oxocentred tetrahedra [OM_4] in the crystal structures of inorganic compounds

S V Krivovichev, S K Filatov, T F Semenova

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Abstract. The crystal structures of inorganic compounds comprising cationic complexes containing oxygen atoms coordinated tetrahedrally to metal atoms, or oxocentred groups [OM_4], are considered. The linking of the [OM_4] tetrahedra in the structures has been analysed and cationic complexes of different structures have been identified. The rules governing the linking of the [OM_4] tetrahedra have been formulated and the cationic complexes have been subjected to a detailed systematic treatment on their basis. Data on the statistics of the bond lengths and bond angles in the [OM_4] tetrahedra are presented. The bibliography includes 317 references.

I. Introduction

One of the approaches to the description of crystal structures is the identification in the latter of cations as the central atoms and of anions as ligands. However, a number of crystal structures can also be considered from the standpoint of the coordination of anions [1–7] and in particular of oxygen atoms (Al_2O, Al_3O,[8,9] Mg_2O, Mg_3O,[10–13] Li_3O, Li_4O, Li_5O,[14,15] Na_3O, Na_4O, K_3O, K_4O,[16,17] *etc*. clusters). Some workers [18–21] have used this approach for the description of crystal structures, identifying in the latter individual atomic groups formed by anions as the central atoms and by cations as the ligands. The development of this approach constitutes the subject of the crystal chemistry of compounds with oxocentred complexes, within the framework of which one considers 'additional' oxygen atoms — atoms which do not enter into the composition of the traditional anionic complexes [T_mO_m] (T = Si, Ge, B, S, P, V, As, Se, *etc*.) and water molecules — as the coordination centres. We emphasise that the proposed method applies only to cationic complexes and does not alter the classification of structures based on the type of anionic groups. In most cases, the 'additional' oxygen atoms are involved in the tetrahedral coordination of metal atoms and oxygen is thus the central atom in cationic $[OM_4]^{n+}$ complexes. We may note that the coordination of the 'additional' oxygen atom in the complex originally studied structurally was not as a rule analysed, but sometimes an oxocentred complex based on [OM_4] groups was identified in connection with the main alternative description of the structure. For example, Sahl [22] described the structure of lanarkite $Pb_2O(SO_4)$ on the basis of chains of [OPb_2], consisting of edge-linked [OPb_4] tetrahedra and sulfate groups [SO_4]. Apparently the first systematic study on this topic is that of Bergerhoff and Paeslack,[19] where the authors specified only 'additional' oxygen atoms as the centres for a series of tetrahedral complexes based on [OM_4] groups. The calculation of the stoichiometric cation/additional oxygen atom ratios, which are sometimes appreciably greater than unity, serves as the crystal-chemical basis for this approach. Thus in the structure of dolerophanite $Cu_2O(SO_4)$,[23,24] the ratio is 2, which provides grounds for considering the 'additional' oxygen atom as the coordination centre. Six oxocentred complexes based on [OM_4] tetrahedra have been identified:[19] a single tetrahedron, a chain, three types of layers, and one framework. Such a small structural diversity of [OM_4] complexes is due to the fact that at the time when the above communication was written [19] (1968) few structures with 'additional' oxygen atoms were known. Later Carre *et al*.[20] analysed a series of compounds with complexes based on oxocentred [OLa_4] tetrahedra. They specified [20] five different types of complexes considered as derivatives of the oxocentred [OLa] layer. Bengtsson and Holmberg [21] published a review on the structural chemistry of crystalline and amorphous media containing [OPb_4] tetrahedra. Oxocentred [OPb_4] tetrahedra have been found in glasses of the $PbO – PbF_2$ system.[25–27] They produce a three-dimensional framework made up of O – Pb – O linkages and performing in essence a function analogous to that of the [SiO_4] tetrahedra in silicate glasses. The [OCu_4] tetrahedra are well known in organometallic chemistry as the central groups in copper(II) μ_4-oxo-complexes.[28–37] Ten types of [OCu_4] complexes have been identified [38–41] and their characteristic features have been noted: the cationic nature of [OM_x] tetrahedral complexes; owing to the large size of the central atom and its relatively low charge (2−), the tetrahedra are linked to one another not only *via* common corners but also *via* their edges and there is also a possibility of corners common to more than two tetrahedra (this accounts for the exceptional diversity of the types of complexes).

S V Krivovichev, S K Filatov, T F Semenova St.-Petersburg State University, Universitetskaya naberezhnaya 7/9, 199034 St.-Petersburg, Russian Federation. Fax (7-812) 218 13 44. Tel. (7-812)218 96 47.
E-mail: flt@cryst.geol.pu.ru (S V Krivovichev)

Received 11 September 1997
Uspekhi Khimii **67** (2) 155 – 174 (1998); translated by A K Grzybowski

Inorganic compounds incorporating an oxygen atom with tetrahedral coordination involving metal atoms are examined in the present review and a systematic crystal-chemical description of the ways in which the oxocentred $[OM_4]$ groups are linked together to form cationic $[O_mM_n]$ complexes is given.

II. The bond lengths in $[OM_4]$ complexes and the physical properties of compounds with $[OM_4]$ tetrahedra

The identification of the oxocentred cationic $[OM_4]$ complexes as structural units of a special type arose because of the high strength of the O – M bonds in these groups. Table 1 presents the average M – O distances (M = Cu, Sn, Pb, La) in structures with tetrahedrally coordinated 'additional' oxygen atoms O_A and the anionic $[TO]_n$ complexes formed by the central atom T and the oxygen atoms O_T as the ligands {$[TO_3]$, T = Se, As; $[TO_4]$, T = S, Cr, V, P, Ge; $[TO_6]$, T = Mo, Re}. Thus the average M – O_A and M – O_T distances are 1.93 and 1.99 Å respectively for M = Cu, 2.23 and 2.42 Å for M = Sn, 2.33 and 2.69 Å for M = Pb, and 2.42 and 2.60 Å for M = La. We may note that bonds longer than 2.1 Å were not taken into account in calculating the Cu – O bond lengths.

The O_A – M bond is on average shorter than O_T – M, which suggests a high bond strength in the oxocentred tetrahedral complexes and influences the physical properties of the chemical compounds.

We shall consider as an example the crystal structure of georgbokiite $Cu_5O_2(SeO_3)_2Cl_2$ (Fig. 1). In this structure, there are isolated groups (SeO_3) with Se atoms involved in ternary 'pyramidal' coordination. According to traditional crystal-chemical ideas, this structure is considered from the standpoint of the coordination of copper and selenium atoms. Three crystallographically nonequivalent copper atoms form coordination polyhedra with different structures and compositions: $Cu(1)O_3Cl_2$ — trigonal bipyramid; $Cu(2)O_4Cl_2$ and $Cu(3)O_5Cl$ — octahedra. Only the equatorial CuO_4 fragments are indicated in Fig. 1*a* for the octahedra as the most stable groups. The $Cu(3)O_4$ squares are linked *via* their edges, forming infinite CuO_2 chains, extended

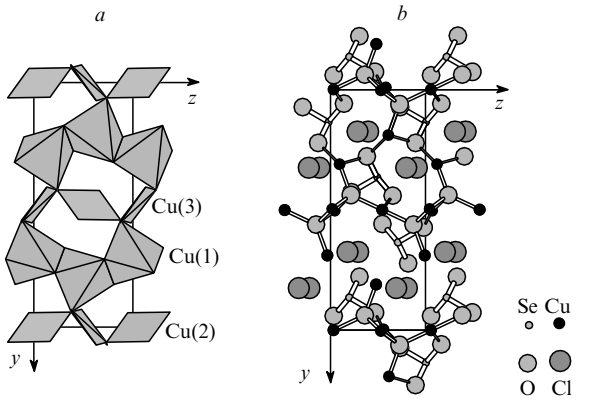


Figure 1. The crystal structure of georgbokiite $Cu_5O_2(SeO_3)_2Cl_2$ in projection onto the *yz* plane.[42]
(*a*) Representation in terms of the coordination polyhedra of copper; (*b*) 'ball-and-stick' representation.

Table 1. The M – O bond lengths for the 'additional' oxygen atom O_A in the $[OM_4]$ tetrahedra and the O_T oxygen atom in the $[TO_3]$ triangular groups, $[TO_4]$ tetrahedra, or $[TO_6]$ octahedra.

Compound	M – O_A /Å	M – O_T /Å	Ref.	Compound	M – O_A /Å	M – O_T /Å	Ref.
M = Cu				M = Pb			
$Cu_5O_2(SeO_3)_2Cl_2$	1.95	2.00	42	$Pb_2O(SO_4)$	2.30	2.66	22
	(1.93 – 1.98)	(1.94 – 2.05)			(2.27 – 2.33	(2.46 – 2.85)	
$KCu_3OCl(SO_4)_2$	1.92	2.01	43, 44	$Pb_3O_2(SO_4)$	2.32	2.80	57, 58
	(1.86 – 1.98)	(1.93 – 2.08)		($P2_1/m$)	(2.18 – 2.43)	(2.69 – 2.95)	
$Cu_2O(SO_4)$	1.92	1.99	23, 24	$Pb_3O_2(SO_4)$	2.36	2.62	59
	(1.88 – 2.00)	(1.91 – 2.07)		(*Cmcm*)	(2.32 – 2.39)	(2.55 – 2.70)	
$NaKCu_3O(SO_4)_3$	1.93	1.97	45	$Pb_3O_2(SO_4)$	2.32	2.76	60
	(1.91 – 1.94)	(1.92 – 2.03)		($P1$)	(2.12 – 2.49)	(2.55 – 2.97)	
$K_2Cu_3O(SO_4)_3$	1.93	1.97	46, 47	$Pb_5O_3(GeO_4)$	2.32	2.54	61
	(1.92 – 1.96)	(1.93 – 2.03)			(2.19 – 2.68)	(2.14 – 2.92)	
$Na_2Cu_4O(PO_4)_2Cl$	1.88	2.00	48	$Pb_{19}(VO_4)_2O_9Cl_4$	2.32	2.77	62, 63
	(1.85 – 1.91)	(1.92 – 2.03)			(2.18 – 2.59)	(2.36 – 3.10)	
$Cu_4O(PO_4)_2$	1.91	1.98	49, 50	$Pb_2O(CrO_4)$	2.30	2.78	64 – 66
	(1.90 – 1.92)	(1.92 – 2.09)			(2.28 – 2.31)	(2.46 – 2.93)	
$Cu_2O(SeO_3)$	1.96	1.97	51	$Pb_8Cu(AsO_3)_2O_3Cl_3$	2.40	2.57	67
($P2_1/n$)	(1.93 – 1.97)	(1.93 – 2.02)			(2.18 – 2.57)	(2.34 – 2.89)	
$Cu_2O(SeO_3)$	1.94	2.02					
($P2_13$)	(1.92 – .97)	(1.98 – 2.08)		M = La			
$Cu_5O_2(PO_4)_2$	1.93	1.96	52	$La_3O_2(ReO_6)$	2.38	2.60	68
	(1.91 – 1.94)	(1.90 – 2.06)		($P2_1/m$)	(2.32 – 2.45)	(2.42 – 2.86)	
$Cu_4O(AsO_4)_2$	1.91	1.97	53	$La_4O_2(Re_2O_8)$	2.41	2.57	69
($P1$)	(1.90 – 1.93)	(1.93 – 2.02)			(2.41)	(2.54 – 2.60)	
$Cu_5O_2(VO_4)_2$	1.94	1.98	54, 55	$La_4O(Mo_2O_{10})$	2.40	2.56	70
	(1.90 – 2.10)	(1.89 – 2.05)			(2.39 – 2.41)	(2.37 – 2.90)	
				$La_3O_2(ReO_6)$	2.39	2.60	71
M = Sn				($C2$)	(2.32 – 2.50)	(2.24 – 3.00)	
$Sn_2O(SO_4)$	2.23	2.42	56	$La_4O(Re_6O_{18})$	2.52	2.65	72
	(2.14 – 2.35)	(2.23 – 2.56)			(2.52)	(2.51 – 2.93)	

Note. The space group is indicated for compounds existing in several polymorphic modifications. The table presents the average bond lengths and the limits of their variation (in brackets) in the crystal structure. The error in the determination of the bond lengths does not exceed 0.01 Å.

along the *x* axis and joined together into a layer parallel to the *xz* plane. The layers are combined into a framework *via* the $Cu(1)O_3Cl_2$ polyhedra. Thus, from the standpoint of traditional ideas, the most stable fragment in the structure of georgbokiite is a chain, parallel to the *x* axis, made up of edge-linked CuO_4 squares. However, in the study of thermal deformations of georgbokiite it was found that the *z* and *y* axes are respectively the directions of minimum and maximum thermal expansions, the average expansion occurring along the *x* axis.[73] Furthermore, one of the cleavage planes (*yz*) in the test compound is perpendicular to the direction of the CuO_2 chains.

Analysis of this structure from the standpoint of the crystal chemistry of oxocentred complexes showed that the 'additional' oxygen atoms are tetrahedrally coordinated to copper atoms (Fig. 1*b*). By being alternately corner- and edge-linked, the [OCu_4] groups form oxocentred [O_2Cu_5] chains extended parallel to the *z* axis (Fig. 2). The thermal expansion is a minimum precisely along this direction and both cleavage systems (*xz* and *yz*) are parallel to the latter. The maximum refractive index, corresponding as a rule to the direction of the densest rows of atoms, corresponds also to the direction of the *z* axis.[74, 75]

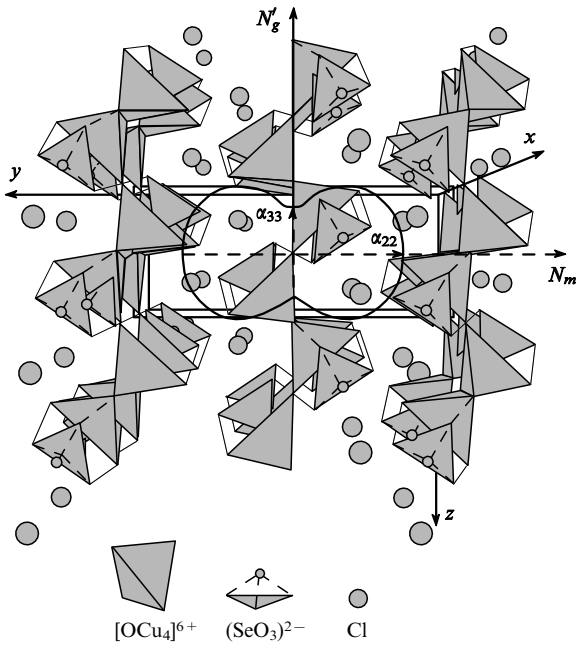


Figure 2. The oxocentred [O_2Cu_5] chains in the structure of georgbokiite and the figure representing its thermal expansions.
α_{22} and α_{33} are the axes of the figure representing the thermal expansion coefficients; N_g' and N_m are the axes of the optical indicatrix in the *yz* plane.

Thus the identification of oxocentred groups in the structures makes it possible to treat more clearly the anisotropy of the thermal expansion and of other physical properties of georgbokiite than in the traditional approach. Henceforth, in numerating the ways in which the [OM_4] groups can be linked together to form a cationic complex, we shall make use of polyhedral images similar to that presented in Fig. 2. Images of the structures from the point of view of the classical approach (Fig. 1) may be found in the original studies indicated in the references.

III. Systematic treatment of cationic complexes based on [OM_4] tetrahedra and the principles governing their descriptions

In traditional crystal chemistry, [TO_4] tetrahedra are as a rule corner-linked and one corner belongs to not more than two tetrahedra.[76, 77] The linking together of the tetrahedra *via* their edges (let alone faces) is encountered very rarely. For example, edge-linking of the tetrahedra in silicate anions has been established in the fibrous modification of silicon dioxide[76] and in certain beryllosilicates.[78] The formation of 'knotted' linkages,[77, 78] *i.e.* the linking together of several tetrahedra by one corner, is also an exceptional case and the 'knot' consists as a rule of not more than four highly distorted tetrahedra.

In describing the crystal structure using [OM_4] tetrahedra, the possibility of their edge-linking is postulated and one M corner can belong to more than two tetrahedra.

In the present review, oxocentred [OM_x] complexes are represented as an assembly of [OM_4] tetrahedra.

There are several classifications of polyhedral structural units.[76, 79, 80] The classification based on Liebau features,[76] constructed on the basis of a traditional systematic treatment of silicates devised by Machatschki, Bragg, *etc*., is the most general. The Liebau classification involves both different geometrical types of coordination polyhedra and various ways of linking them together (*via* corners, edges, and *n*-corner faces). However, it bears features of the structure of silicate anions, for the classification of which it has in fact been created. For a more complete classification of polyhedral edge-linked and face-linked structural units, this system requires a series of amplifications, which are unimportant for silicates. The principal characteristics of the systematic treatment employed are described briefly below and an account is given of the main principles governing this description of structures made up of oxocentred fragments. The problems of the classification of polyhedral structures have been described in greater detail in another communication.[81]

Features of the systematic treatment. 1. The coordination of the central atom is a parameter which includes both the coordination number of the central atom and the geometry of the coordination polyhedron. The recommendations given by Parthé and coworkers[79, 80, 82] are employed in the determination of the values of the parameters. In particular, the designation 4*t* was adopted for tetrahedral groups.

2. The dimensionality of the complex *D* is the number of dimensions in which the complex is of infinite extent. The following values are possible: 0 (finite complexes), 1 (chain complexes), 2 (layered complexes), 3 (framework complexes).

3 and 4. The linkedness of the tetrahedra in the complex *ML* and the linkedness of the tetrahedron *L*.

The parameter *ML* indicates the way in which it is possible to construct the specified complex by adding individual single polyhedra. It is determined as the following hierarchical series of values: $3 > 2$, $3 > 1$, 2, $3 > 1$, $3 > 2 > 1$, $2 > 1 > 0$. Here it is necessary to make use of Wells's rule: if an edge (or face) is shared by two tetrahedra, then its corners (and edges) are not considered to be shared by these two tetrahedra. The value of *L* reflects all the ways of linking together the polyhedra in the complex. The linkedness *L* is equal to the number of corner atoms shared by two coordination polyhedra:[10] $L = 0$ for an isolated polyhedron, $L = 1$ for corner-linking, $L = 2$ for edge-linking, and $L = 3$ and above for face-linking.

5. The connectedness *s* of the polyhedra of a coordination polyhedron is equal to the number of polyhedra with which the given polyhedron shares corners, regardless of their linkedness.[76, 82]

6. The branchedness of the complex *B*. The finite structural units and single chains † are called unbranched if they contain no subunits linked to more than two other subunits.[82] Otherwise they are called branched. Furthermore, complex structural complexes, which may be regarded as made up of unbranched (branched) finite fragments or unbranched (branched) single chains, are described as unbranched (branched). The branchedness *B* of a cationic complex of infinite extent (*i.e.* with $D > 0$) is a property of its fundamental chain. The fundamental chain is defined as the

† A chain consisting of secondary tetrahedra is called single.

chain from which the cationic complex may be constructed by its successive addition.[82] The fundamental chain consists of a single chain (made up of only secondary polyhedra) and branches. Liebau[76] suggested that unbranched, open-branched, loop-branched, mixed-branched, and hybrid complexes, designated respectively by the symbols *uB*, *oB*, *lB*, *olB*, and *hB*, be distinguished.

7. The periodicity *P*. The term periodicity of a structural fragment of infinite extent is the number of structural subunits (excluding branches) constituting the period of the chain from which this fragment may be constructed by the successive addition of subunits to one another.[82] For finite ring complexes, the number of polyhedra constituting the ring is specified as the periodicity. Liebau[76] calls this parameter the ring periodicity.

8. The multiplicity *M* of the complex is the term given to the number of single polyhedra, chains, or layers, which, by linking to one another, form a complex with the same dimensionality as the initial complexes.[82]

9. The ratio $n:m$ for the complex $[A_nB_m]$, where A is the central atom and B is the ligand.

Formula and diagram of connectedness. The following is the connectedness formula: $(s: L_{1-s_1}; L_{2-s_2}...L_{n-s_n})$, where L_1, L_2, ..., L_n are specific values of linkedness, while s_1, s_2, ... s_n are specific values of connectedness for the given polyhedron with others in accordance with the values of linkedness indicated ahead of them. The formula of the connectedness of this polyhedron shows how many polyhedra are linked to the given polyhedron and in what way. It is convenient to employ the so called diagram of connectedness constructed on the basis of the Schlegel diagram for the given polyhedron. The latter represents a planar image of the edge network of any kind of convex polyhedron. For the tetrahedron, the Schlegel diagram represents the view from above on to a regular tetrahedron placed on one of its triangular bases. The Schlegel diagrams were first introduced into crystal chemistry by Hoppe and Köhler.[83]

Henceforth we shall use the following ways of representing the elements of connectedness.

1. The corner designated by a circle links the given polyhedron to another. If the corner links the given polyhedron to more than one other polyhedron, then the number of such polyhedra is indicated next to the corner.

2. The edge identified by a semibold line is common to two polyhedra.

The connectedness diagrams will be referred to as equivalent if the relative disposition of the linkage corners and/or edges in them is the same (or is mirror-symmetrical).

Classification of the polyhedra in a polyhedral complex. For the crystal-chemical description of the coordination polyhedra, constituting the given complex it is necessary not only to indicate the geometrical characteristics but also to define the way in which they are joined together. Wells[84–86] suggested that polyhedra with the same relative disposition as the elements of connectedness be referred to as topologically equivalent. Within the framework of the approach employed, this means that polyhedra with equivalent connectedness diagrams are referred to as topologically equivalent polyhedra in the complex.

It is essential to note that the description of the disposition of the elements of connectedness in the polyhedron (with the aid of the connectedness diagram) is still insufficient to define the position of the polyhedron in the complex. In the same structure, topologically equivalent polyhedra may have different environments comprising polyhedra with which they have common linkage corners. In such cases we speak of configurationally nonequivalent polyhedra (more rigorous definitions have been given elsewhere[81]).

Configurationally equivalent polyhedra are always topologically equivalent, but topologically equivalent polyhedra may be configurationally nonequivalent. Crystallographically equivalent polyhedra are always topologically and configurationally equivalent.

Thus, from this standpoint, a polyhedral cationic complex consists of *n* types of configurationally equivalent and *m* classes of topologically equivalent polyhedra. In the general case, we have $m < n$. The classification of the polyhedra in the structure is based on the order of hierarchical equivalence ratios: configurational–topological–crystallographic.

Additional features of the systematic treatment. 10. The number of configurational types of polyhedra in the complex and their ratio.

11 and 12. The diagrams and formulae of the connectedness of the configurational types of polyhedra.

Crystal-chemical formulae. When the formula of the complex is written, the system recommended by Liebau *et al.*[76, 82] is used to characterise it structurally. The following parameters are indicated in braces before the chemical formula of the complex written in square brackets: $\{B, M_\infty^D\}$. The following designations are adopted for finite structures ($D = 0$): $\{f\}$ — for a chain of finite length, $\{r\}$ — for a ring polyion, $\{c\}$ — for a cage.[79, 82]

IV. Types of cationic $[OM_4]$ complexes

1. General remarks

The structures of oxocentred complexes are described in terms of the $[OM_4]$ tetrahedra in accordance with the following main principles. Taking into account the features of the classification formulated in the previous section, the type units of oxocentred $[OM_4]$ structural units are treated systematically. All the known crystal structures in which the complex has been found are indicated for complexes of each type. Some of these structures are considered as examples and are described from the standpoint of the crystal chemistry of compounds with oxocentred groups.

For convenience we introduced a numbering of the types of structural units within each dimensionality. A capital Latin letter is placed before the number of the complex indicating its dimensionality: *I* — finite (*islands*), *C* — one-dimensional or chain (*chains*), *L* — two-dimensional or layered (*layers*), *F* — three-dimensional or framework (*frameworks*).

2. Finite oxocentred complexes.

Tables 2 and 3 as well as Fig. 3 present the main types of finite oxocentred complexes, the crystal structures in which these complexes have been found, and a topological description of the latter.

***I*1**. The individual $[OM_4]$ tetrahedron. The oxocentred $[OM_4]$ tetrahedron is known in organic crystal chemistry,[28–37] for example M = Cu, Be, or Zn. Among inorganic compounds, a single $[OM_4]$ tetrahedron can be identified, in particular, in the crystal structure of ponomarevite $K_4Cu_4OCl_{10}$,[87–89] which con-

Table 2. Classification of the types of finite oxocentred complexes based on the $[OM_4]$ tetrahedron.

Number	*L*	Parameter	*n*	O : M	Type of complex	*m*	*p*	Connectedness formula
*I*1	0	–	1	1 : 4	$[OM_4]$	1	1	(0)
*I*2	1	$\{f\}$	2	2 : 7	$\{f\}[O_2M_7]$	1	1	(1: 1 – 1)
*I*3	1	$\{f\}$	4	4 : 3	$\{f\}[O_4M_{13}]$	2	A1	(1: 1 – 1)
							B1	(2: 1 – 2)
*I*4	2	$\{f\}$	2	1 : 3	$\{f\}[O_2M_6]$	1	1	(1: 2 – 1)
*I*5	2	$\{f\}$	4	2 : 5	$\{f\}[O_4M_{10}]$	2	A1	(1: 2 – 1)
							B1	(2: 2 – 2)
*I*6	2	$\{c\}$	4	1 : 2	$\{c\}[O_4M_8]$	1	1	(3: 2 – 3)

Note. The following designations have been adopted here and in the subsequent tables: n = number of tetrahedra in the complex, m = number of topological types of tetrahedra in the complex, p = number of tetrahedra of the given topological type (A and B) in the complex.

Table 3. Finite oxocentred [OM_4] complexes in the crystal structures of inorganic compounds.

Number	Type of complex	Chemical formula of complex	Chemical compound	Ref.
*I*1	[OM_4]	[OCu_4]	$K_4Cu_4OCl_{10}$ (ponomarevite)	87–89
			$Cu_4(PO_4)_2O$	49–50
			$CuO(Cu,Mg)_3(As_xP_{1-x}O_4)_2$ ($x = 0.3$)	90
			$Cu_4(AsO_4)_2O$, *P*1	53
			$Cu_4(AsO_4)_2O$, *Pnma*	91
			$KCu_5V_3O_{13}$	92
			$Cu_{11}O_2(VO_4)_6$ (fingerite)	93
		[OZn_4]	$Zn_4O(BO_2)_6$	94
		[OPb_4]	$Pb_4O(Pb_2(BO_3)_3Cl)$	95
			$Pb_8Bi_2(PO_4)_6O_2$	96
		[$OKBi_3$]	$K_2Bi_3(PO_4)_2O$	97
		[OYb_4]	Yb_4OCl_6	98
		[OSm_4]	Sm_4OCl_6	99
		[OEu_4]	Eu_4OCl_6	100
		[OLa_4]	$(La_4O)(Re_6O_{18})$	72
			$La_4Mo_2O_{11}$	70
		[OCa_4]	Ca_4OCl_6	101
			$Ca_4(PO_4)_2O$	102
		[OFe_4]	$Fe_{15}Ge_8O_{36}$	103
		[OCe_4]	$Ce_4OS_4Cl_2$	104
		[OM_4] (M = La–Nd)	$M_4OS_4Cl_2$ (M = La–Nd)	105
*I*1	[OM_4]	[OLa_2Ga_2]	$La_2ZnGa_2S_6O$	106
		[$OCaLaGa_2$]	$CaLaGa_3S_6O$	106
		[$OSrLaGa_2$]	$SrLaGa_3S_6O$	106
		[OSr_2Ge_2]	$Sr_2ZnGe_2S_6O$	106
*I*2	{*f*}[O_2M_7]	[O_2Pb_7]	$Pb_9Al_8O_{21}$	107
			$Pb_9Ga_8O_{21}$	108, 109
		[O_2Pb_6Sb]	$Pb_6Cu_4AlSbO_2(OH)_{16}Cl_4 \cdot (SO_4)_2$ (mammothite)	110
		[O_2Cu_7]	$Cu_9O_2(PO_4)_4(OH)_2$	111
		[$O_2TiFe_3Ba_3$]	$Ba_4Fe_3Ti(B_2Si_8O_{27})O_2Cl_{0.89}$ (taramellite)	112, 113
*I*3	{*f*}[O_4M_{13}]	[O_4Cu_{13}]	$Cu(Cu_{13}O_4)(SeO_3)_2Cl_{16}$	114
*I*4	{*f*}[O_2M_6]	[O_2Zn_6]	$Zn_4V_2O_9$	115
		[O_2Pb_6]	$Pb_3MO_{12}F_2$ (M = Nb, Ma)	116
		[O_2Fe_6]	$Fe_{3.2}Ge_{1.8}O_8$	117
		[O_2Cu_6]	$K_2Cu_3O(SO_4)_3$ (fedotovite)	46, 47
			$NaKCu_3O(SO_4)_3$ (euchlorine)	45
			$Cu_4O(SeO_3)_3$-I,II	51
*I*5	{*f*}[O_4M_{10}]	[$O_4Sr_4Bi_6$]	$Sr_2Bi_3V_3O_{14}$	118
*I*6	{*c*}[O_4M_8]	[O_4Pb_8]	$Pb_9O_4Br_9$	119
			$TlPb_8O_4Br_9$	120
		[O_4Sn_8]	$Sn_2O(SO_4)$	56

tains tetranuclear clusters [Cu_4OCl_{10}] formed by oxygen as the central atom involved in tetrahedral coordination.

***I*2**. The binary group {*f*}[O_2T_7]. This oxocentred complex consists of two [OM_4] tetrahedra linked by one common corner and it is therefore 'reverse' analogue of the diorthosilicate group [Si_2O_7].

***I*3**. The chain fragment {*f*} [O_4M_{13}] made up of four tetrahedra and discovered in the crystal structure of the compound $Cu(Cu_{13}O_4)(SeO_3)_2Cl_{16}$.[114] The fragment consists of four [OCu_4] tetrahedra linked in succession *via* their corners. In the structure of

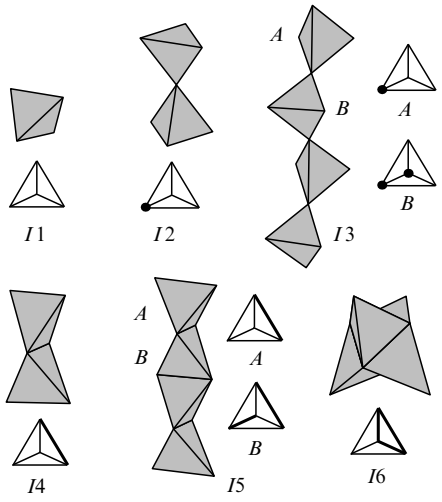


Figure 3. The types of finite oxocentred complexes.
A, *B* — tetrahedra belonging to different topological types.

the given compound, there are copper atoms which do not enter into the oxocentred tetrahedra.

***I*4**. The binary group {*f*} [O_2M_6] consists of two tetrahedra having one common edge. The presence of the complex [O_2Cu_6] having this structure has been established in the crystal structure of the exhalation mineral fedotovite $K_2Cu_3O(SO_4)_3$.[46,47]

***I*5**. We identified the chain fragment {*f*}[O_4M_{10}] with an edge-linkage made up of four tetrahedra in the crystal structure of $Sr_2Bi_3V_3O_{14}$ solved by Boje and Müller-Buschbaum.[118] From the standpoint of the approach employed, the formula of this compound is written as $Sr_2Bi_3O_2(VO_4)_3$.

***I*6**. An oxocentred complex made up of four [OM_4] tetrahedra in which each tetrahedron is edge-linked to three others, was first noted by Keller in the compounds $Pb_9O_4Br_9$[119] and $TlPb_8O_4Br_9$.[120] Later Riebe and Keller [121] noted that in a complex having this structure the M atoms not involved in the linking of the tetrahedra may be replaced by hydrogen.

It is of interest that the complex [O_4Pb_4], having a similar structure but incorporating only Pb atoms participating in the linking of the tetrahedra, has been discovered in the gas phase,[128,129] while the complexes [$(OH)_4M_4$] (M = Mg, Co, Ni, Cd, Pb) have been found in aqueous solutions.[130–132]

Table 4 presents the finite complexes formed from the complex *I*6 for different degrees of substitution *n*.

Table 4. Finite oxocentred complexes formed from complex *I*6 as a result of the substitution $n(O + M) \rightarrow n(OH)$.

n	Type of complex	Chemical formula of complex	Chemical compound	Ref.
0	{*c*}[O_4M_8]	[O_4Pb_8]	$Pb_9O_4Br_9$	119
			$TlPb_8O_4Br_9$	120
		[O_4Sn_8]	$Sn_2O(SO_4)$	56
1	{*c*}[$O_3(OH)M_7$]	[$O_3(OH)Sn_7$]	$Sn_{21}Cl_{16}(OH)_{14}O_6$	122, 123
2	{*c*}[$O_2(OH)_2M_6$]	[$O_2(OH)_2Pb_4Hg_2$]	$HgPb_2O(OH)Br_3$	121
4	{*c*}[$(OH)_4M_4$]	[$(OH)_4Pb_4$]	$Pb_4(OH)_4(ClO_4)_4 \cdot 2H_2O$	124
			$[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10} \cdot 2H_2O$	125
		[$(O,OH)_4Pb_4$]	$Pb_7Ca_2Al_{12}Si_{36}(O,OH)_{100} \cdot m(H_2O,OH)$	126, 127

3. Oxocentred chain complexes

Oxocentred chains can be conveniently classified in terms of the types of single chains from which they are constructed. The linking of single chains leads to the formation of multiple structural units. All the oxocentred chains can be divided into families in terms of their multiplicity and linkedness. Tables 5 and 6 present the types of oxocentred chain complexes based on the $[OM_4]$ tetrahedra and the chemical compounds in the structures of which such complexes have been found.

Table 5. Classification of the types of oxocentred chain complexes based on the [OM_4] tetrahedron.

Number	*ML*	*L*	*P*	*B*	*M*	O : T	*n*	*m*	*p*	Connectedness formula
*C*1	1	1	1	*uB*	1	1 : 3	1	1	1	(2: 1 – 2)
*C*2	1	1	1	*uB*	2	2 : 5	1	1	1	(3: 1 – 3)
*C*3	2	1, 2	1	*uB*	2	1 : 2	1	1	1	(4: 1 – 2; 2 – 2)
*C*4	2	1, 2	1	*uB*	3	3 : 5	2	2	*A*2	(5: 1 – 3; 2 – 2)
									*B*1	(6: 1 – 2; 2 – 4)
*C*5	1	1	2	*uB*	1	1 : 3	1	1	1	(2: 1 – 2)
*C*6	1, 2	1, 2	2	*uB*	2	2 : 5	2	2	*A*1	(3: 1 – 3)
									*B*1	(4: 1 – 3; 2 – 1)
*C*7	2	2	2	*uB*	1	1 : 2	1	1	1	(2: 2 – 2)
*C*8	2	1, 2	2	*uB*	2	2 : 3	1	1	1	(5: 1 – 2; 2 – 3)
*C*9	2	1, 2	2	*uB*	3	3 : 4	2	2	*A*1	(5: 1 – 2; 2 – 3)
									*B*2	(8: 1 – 4; 2 – 4)
*C*10	2	1, 2	2	*uB*	6	6 : 7	3	3	*A*1	(7: 1 – 4; 2 – 3)
									*B*1	(9: 1 – 6; 2 – 3)
									*C*1	(13: 1 – 8; 2 – 5)
*C*11	2	1, 2	2	*uB*	6	6 : 7	5	4	*A*1	(5: 1 – 2; 2 – 3)
									*B*1	(12: 1 – 8; 2 – 4)
									*C*2	(9: 1 – 6; 2 – 3)
									*D*1	(18: 1 – 12; 2 – 6)
									*E*1	(9: 1 – 6; 2 – 3)
*C*12	1, 2	1, 2	2	*uB*	1	2 : 5	1	1	1	(2: 1 – 1; 2 – 1)
*C*13	1, 2	1, 2	2	*uB*	2	1 : 2	2	2	*A*1	(3: 1 – 2; 2 – 1)
									*B*1	(4: 1 – 2; 2 – 2)
*C*14	1, 2	1, 2	4	*uB*	1	2 : 5	1	1	1	(2: 1 – 1; 2 – 1)
*C*15	1, 2	1, 2	6	*uB*	1	3 : 8	2	2	*A*1	(2: 1 – 2)
									*B*2	(2: 1 – 1; 2 – 1)
*C*16	1	1	1	*lB*	2	1 : 2	3	3	*A*1	(4: 1 – 1; 2 – 3)
									*B*2	(3: 1 – 2; 2 – 1)
									*C*1	(4: 1 – 3; 2 – 1)

***C*1**. The single-period chain $\{uB, 1^1_\infty\}[OM_3]$ (Fig. 4). In this chain, the tetrahedra are linked only *via* the corners with a periodicity 1. This polyion is an analogue of the metagermanate chain $[GeO_3]$.

***C*2**. The $\{uB, 2^1_\infty\}[O_2M_5]$ double chain. The linking of two *C*1 chains *via* free corners leads to the formation of the *C*2 double chain. Such a fragment can be identified in chemical compounds belonging to the ludwigite structural type. In the crystal structures of these compounds, there is also an 'additional' oxygen atom with a tetragonal-pyramidal coordination, as well as metal atoms which do not enter into the tetrahedral oxocentred complex.

***C*3**. The $\{uB, 2^1_\infty\}[OM_2]$ double chain. The linking of two *C*1 chains to one another *via* the edges leads to the formation of a type *C*3 oxocentred chain. The main type of linkedness *ML* for this double chain is 2, although for the fundamental chain *ML* = 1. The *C*3 chain may be identified in oxoborates with the warwickite structural type. In contrast to ludwigite, in the warwickite structural type all the 'additional' oxygen atoms are involved in tetrahedral coordination and all the metal atoms enter into the oxocentred complex. Chains of analogous structure have been found in the structures of the diorthosilicates of the cuspidine and epistolite groups (innelite, lomonosovite, murmanite, *etc.*). In such compounds, the 'additional' oxygen, not entering into anionic complexes, may be substituted by fluorine with its similar properties. The nature of the substitution can be both statistical and ordered. The structural similarity of oxoborates and the cuspidine-group diorthosilicates was first pointed out by Belov.[77]

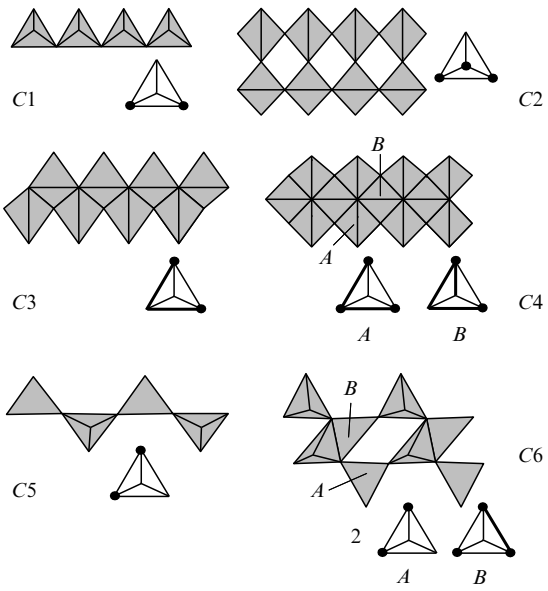


Figure 4. The types of oxocentred chain complexes (*C*1 – *C*6). *A*, *B* — tetrahedra belonging to different topological types.

***C*4**. The $\{uB, 3^1_\infty\}[O_3M_5]$ triple chain. As a result of the addition of yet another single *C*1 chain to a *C*3 chain, a triple oxocentred *C*4 chain is formed. Such a chain was first identified by Carre *et al.*[20] in the crystal structure of $In_6La_{10}O_6S_{17}$.[180]

The *C*1, *C*3, and *C*4 chains may be assigned to a single family with the general formula $\{uB, n^1_\infty\}[O_nM_{n+2}]$, where *n* is the multiplicity of the chain.

***C*5**. The $\{uB, 1^1_\infty\}[O_2M_6]$ single chain. This chain is topologically equivalent to the *C*1 chain, different from the latter by the periodicity (*P* = 2). In terms of its structure, the *C*5 chain is a reverse analogue of the pyroxene chain in the silicate. The difference consists in the fact that the corners not involved in the linking of the tetrahedra into the *C*5 chain are turned in opposite directions relative to the plane of the chain, whereas in pyroxenes they are turned in one direction. A *C*5 complex has been detected, in particular, in the crystal structure of the exhalation mineral kamchatkite $KCu_3O(SO_4)_2Cl$ (Fig. 5).[43, 44]

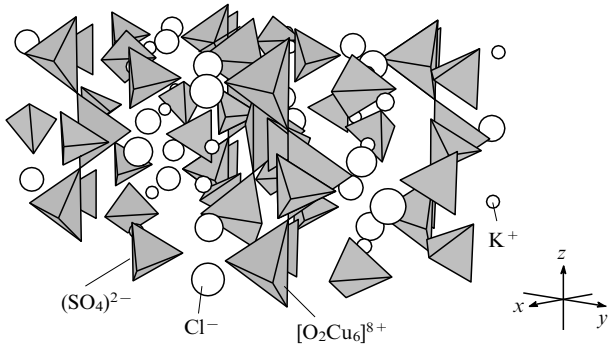


Figure 5. The crystal structure of kamchatkite $KCu_3O(SO_4)_2Cl$.

***C*6**. The $\{uB, 2^1_\infty\}[O_2M_5]$ double chain consists of two edge-linked *C*5 chains. A complex with this structure may be identified in stoiberite $Cu_5O_2(VO_4)_2$,[54, 55] the structure of which was not previously considered in terms of this aspect.

Table 6. Oxocentred [OM_4] chain complexes in the crystal structures of inorganic compounds.

Number	Type of complex	Chemical formula of complex	Chemical compound	Ref.
*C*1	$\{uB, 1^1_\infty\}[OM_3]$	$[OPb_3]$	$Pb_3Ta_5O_9F_{13}$ ($Pb_3O(Ta_5O_8)F_{13}$)	133
		$[OY_3]$	$Y_3OCl_2(OH)_5$	134
		$[OGd_3]$	$Gd_3O(OH)_5Br_2$	135
		$[OCu_2Zn]$	$Cu_2Zn(B_2O_5)O$	136
		$[OCu_2Cd]$	$Cu_2Cd(B_2O_5)O$	137
		$[OCu_2Co]$	$Cu_2Co(B_2O_5)O$	138
*C*2	$\{uB, 2^1_\infty\}[O_2M_5]$	$[O_2M_5]$ (M = Fe, Mg, Ti, Sb, Sn, Ni, Cr, Mn, Al, Mo, Zn	$(Mg,Fe^{2+})_2Fe^{3+}O_2(BO_3)$ (ludwigite)	139 – 143
			$Fe_3O_2(BO_3)$ (vonsenite)	144, 145
			$Mg_{1.7}Mn_{1.29}O_2(BO_3)$ (takeuchiite)	146
			$(Mg,Mn)_2(Mn,Fe)O_2(BO_3)$ (orthopinakiolite)	147
			$(Sn,Fe,Mg)(Fe,Mg)_2O_2(BO_3)$ (hulsite)	148, 149
			$Ni_2CrO_2(BO_3)$	140
			$Ni_2VO_2(BO_3)$	140
			$Ni_2MO_2(BO_3)$ (M = Ga, Fe,Al, Cr)	150
			$Ni_2FeO_2(BO_3)$	151
			$Mg_2MnO_2(BO_3)$ (fredrikssonite)	152
			$Zn_5Mn(BO_3)_2O_4$	153
*C*3	$\{uB, 2^1_\infty\}[OM_2]$	$[OLa_2]$	$(La_2O)(LaGaS_5)$	154
		$[OPb_2]$	$Pb_{11}Si_3O_{17}$	155
			$Pb_{11}Ge_3O_{17}$	156
		[OLaCr]	$LaCrOS_2$	157
		$[OY_2]$	$Y_2O(BeO_3)$	158, 159
		$[OFe_2]$	$Fe_2O(BO_3)$	160
		[OFeCo]	$FeCoO(BO_3)$	158
		$[OMg_{1.5}Ti_{0.5}]$	$Mg(Mg_{0.5}Ti_{0.5})O(BO_3)$ (warwickite)	161 – 163
		$[OMn_2]$	$Mn_2O(BO_3)$	164
		[OMnFe]	$MnFeO(BO_3)$	165
		[OMn(Al,Y)]	$MnAl_{0.5}Y_{0.5}O(BO_3)$	165
		$[OCo_{1.5}M_{0.5}]$ (M = Ti, Zr)	$Co_{1.5}M_{0.5}O(BO_3)$ (M = Ti, Zr)	166
		[OZnFe]	$ZnFeO(BO_3)$	153
		[OTiNa]	$Na_5Ti_2(Si_2O_7)(PO_4)O_2$ (lomonosovite, β-lomonosovite)	167 – 170
			$Na_2Ti_2(Si_2O_7)O_2$ (murmanite)	171, 172
		$[O_3FCa_7Nb]$	$Ca_7Nb(Si_2O_7)_2O_3F$ (niocalite)	173, 174
		$[(O,F)_2Ca_2NaZr]$	$Ca_2Na(Zr,Nb)(Si_2O_7)(O,F)_2$ (woehlerite)	175
		$[(OH,F)Ca_2]$	$Ca_4(Si_2O_7)(OH,F)_2$ (cuspidine)	176, 177
		$[OF(Na,Ca)_3Zr]$	$(Na,Ca,Mn)_3(Zr,Ti)(Si_2O_7)OF$ (lavenite)	178, 179
*C*4	$\{uB, 3^1_\infty\}[O_3M_5]$	$[O_3La_5]$	$In_6La_{10}O_6S_{17}$	180
*C*5	$\{uB, 1^1_\infty\}[O_2M_6]$	$[O_2Cu_6]$	$KCu_3O(SO_4)_2Cl$ (kamchatkite)	43, 44
			$Cu_3V_2O_8(H_2O)$	181
			$Cu_8ZnO_2(SeO_3)_4Cl_6$	182
			$Cu_3Mo_2O_9$	183, 184
			$Na_2Cu(Cu_3O)(PO_4)_2Cl$	48
		$[O_2Zn_6]$	$Zn_3O(SO_4)$	185
		$[O_2Ti_2Y_4]$	$Y_2(Y_2TiO)(SiO_4)_2F_6$	186
*C*6	$\{uB, 2^1_\infty\}[O_2M_5]$	$[O_2Cu_5]$	$Cu_5V_2O_{10}$ (stoiberite)	54, 55
*C*7	$\{uB, 1^1_\infty\}[OM_2]$	$[OPb_2]$	Pb_2OFX (X = Cl, Br, I)	187
			$Pb_2O(SO_4$ (lanarkite)	22
			$Pb_2O(WO_4)$	188
			$Pb_2O(CrO_4)$ (phoenicochroite)	64 – 66
			$Pb_2O(XO_4)$ (X = S, Cr, Mo)	66
		$[O_2Cu_3(Al,Fe)]$	$K_3Cu_3(Al,Fe)O_2(SO_4)_2$ (kljuchevskite)	189, 190
		$[O_2Cu_3Al]$	$K_3Cu_3AlO_2(SO_4)_2$ (alumokljuchevskite)	191
		$[OCu_2]$	$K_2Cu_2O(SO_4)$ (piypite)	192, 193
			$Cu_4O_2(VO_4)Cl$	194
		$[OBi_2]$	$(UO_2)Bi_4O_4(AsO_4)_2 \cdot 2H_2O$ (walpurgite, orthowalpurgite)	195 – 197
		[OPbGe]	$PbGeO(Ge_2O_6)$	198
		[OCaBi]	$CaBiVO_5$	199
		$[OLa_2]$	$La_4Re_2O_{10}$	69
		$[ONd_2]$	$Nd_4Re_2O_{11}$	200
		$[O_2Pr_4]$	$Na_2(Pr_4O_2)Cl_9$	201

Table 6 (continued).

Number	Type of complex	Chemical formula of complex	Chemical compound	Ref.
*C*8	$\{uB, 2^1_\infty\}[O_2M_3]$	$[O_2Pb_3]$	$Pb_3O_2(SO_4)$ ($P2_1/m$)	57, 58
			$Pb_3O_2(SO_4)$ ($Cmcm$)	59
			$Pb_3O_2(SO_4)$ ($P1$)	60
			$Pb_3O_2Cl_2$ (mendipite)	202, 203
			$Pb_3O_2I_2$	204
			$Pb_3CuO_2(OH)_2Cl_2$ (chloroxiphite)	205
		$[O_2BiMg_2]$	$BiMg_2O_2(PO_4)$	206
			$BiMg_2O_2(AsO_4)$	
		$[O_2La_3]$	$La_3O_2(ReO_6)$ ($P2_1/m$)	68
			$La_3O_2(ReO_6)$ ($C2$)	69
		$[O_2Y_3]$	$Y_3O_2(ReO_6)$	207
		$[O_2Sm_3]$	$Sm_3O_2(ReO_6)$	208
		$[O_2Ce_2Ti]$	$Na_2Ce_2TiO_2(SiO_4)(CO_3)_2$ (tundrite)	209, 210
*C*9	$\{uB, 3^1_\infty\}[O_3M_4]$	$[O_3La_4]$	$La_4O_3(AsS_3)_2$	211
*C*10	$\{uB, 6^1_\infty\}[O_6M_7]$	$[O_6Bi_7]$	$Bi_{14}O_{16}(SO_4)_5$	212
*C*11	$\{uB, 6^1_\infty\}[O_6M_7]$	$[O_6Bi_7]$	γ-Bi_2MoO_6	213
*C*12	$\{uB, 1^1_\infty\}[O_2M_5]$	$[O_2Cu_5]$	$Cu_2O_5(SeO_3)_2Cl_2$	42
			$Cu_5O_2(PO_4)$	52
		$[O_2M_5]$ (M = Pb, Ge,	$Pb_3GeGa_{10}O_{20}$	214
		Ga, Ba, Al, Sn, Fe, Ti	$Ba_3SnFe_{10}O_{20}$	214
			$Pb_3GeAl_{10}O_{20}$	215
			$Pb_3SiAl_{10}O_{20}$	215
			$Ba_3TiAl_{10}O_{20}$	216
			$BaSrPbMn_2Al_9O_{20}$	217
*C*13	$\{uB, 2^1_\infty\}[OM_3]$	$[OAl_2]$	$Al_2O(SiO_4)$ (kyanite)	218, 219
		$[OFe_2]$	$Fe_2O(GeO_4)$	220
*C*14	$\{uB, 1^1_\infty\}[O_2M_5]$	$[O_2(Mg,Fe)_5]$	$Na_2(Mg,Fe)_6[(Ge,Fe)_6O_{18}]O_2$	221
		$[O_2(Mg,Cr)_5]$	$NaMg_2Cr(Si_3O_9)O$ (krinovite)	222
		$[O_2(Mg,Al)_5]$	$Ca_2(Mg,Al)_6O_2[(Si,Al,B)_6O_{18}]$ (serendibite)	223 – 225
		$[O_2(Fe,Ti)_5]$	$Na_2Fe_5TiO_2(Si_6O_{18})$ (aenigmatite)	226
		$[O_2(Mg,Ti,Al,Fe)_5]$	$Ca_2(Mg,Ti,Al,Fe)_6O_2(Si_6O_{18})$ (rhoenite)	227
			$(Ca,Na)_2(Mg,Al,Fe)_6O[(Si,Al,Be)_6O_{18}]$ (makarochkinite)	228
*C*15	$\{uB, 1^1_\infty\}[O_3M_8]$	$[O_3Pb_8]$	$Pb_8Cu(AsO_3)_2O_3Cl_5$ (freedite)	67, 229
*C*16	$\{lB, 2^1_\infty\}[OM_2]$	$[O_3Cu_4Ti_2]$	$Cu_9Ti(B_2O_5)(BO_3)_2O_6$	230

***C*7**. The $\{uB, 1^1_\infty\}[OM_2]$ fundamental chain (Fig. 6). A single oxocentred chain, consisting of secondary tetrahedra edge-linked in succession, was first identified by Sahl [22] in the crystal structure of lanarkite $Pb_2O(SO_4)$. This one-dimensional structural unit based on $[OM_4]$ tetrahedra is one of the commonest in oxocentred complexes. Thus it has been detected in three new minerals of exhalation origin in the Tolbachick volcano: klyuchevskite,[189, 190] alumoklyuchevskite,[191] and piypite.[192, 193]

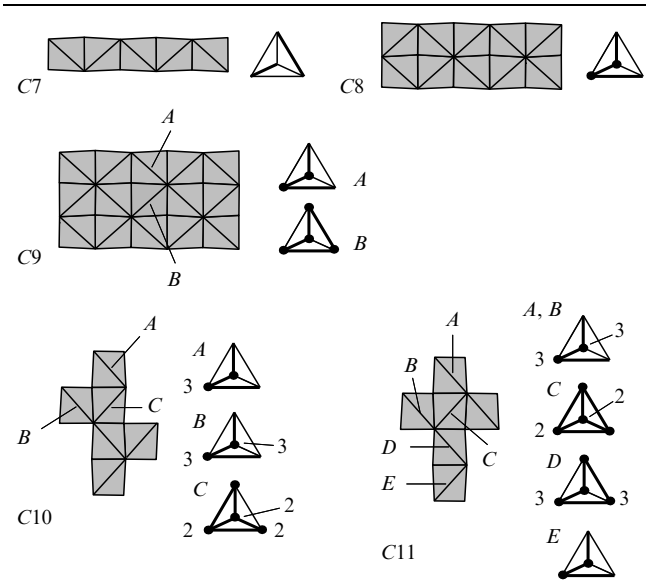


Figure 6. The types of oxocentred chain complexes (*C*7 – *C*11). *A*, *B*, *C*, *D*, *E* — tetrahedra belonging to different topological types.

***C*8**. The $\{uB, 2^1_\infty\}[O_2M_3]$ double chain. The edge-linking of two *C*7 chains leads to the formation of the *C*8 double chain.

***C*9**. The $\{uB, 3^1_\infty\}[O_3M_4]$ triple chain is formed by the linking of three *C*7 chains. A similar complex with the formula $[O_3La_4]$ has been identified by Carre *et al.*[20] in the crystal structure of $La_4O_3As_3S_9$.[211]

The *C*7, *C*8, and *C*9 chains form a family with the general formula $\{uB, n^1_\infty\}[O_nM_{n+1}]$, where n is the multiplicity of the chain. It may be postulated that a chain belonging to the same family with $n = 4$ occurs in the crystal structure of $Pb_5O_4[SO_4]$, which could not be fully solved. This hypothesis is based on the existence of oxocentred chains of type *C*7 ($n = 1$) and *C*8 ($n = 2$) in the compounds $Pb_2O(SO_4)$ [22] and $Pb_3O_2(SO_4)$ [57 – 60] respectively, which have similar compositions.

***C*10**, ***C*11**. The six-fold chains having the general formula $\{uB, 6^1_\infty\}[O_6M_7]$ consist of six type C7 chains linked in different ways. The possibility of identifying the *C*10 polyion in the $Bi_{14}O_{16}(SO_4)_5$ structure and of representing it by a block cut out of a type PbO layer was pointed out by Aurivillius.[212] The *C*11 chain may be identified in the structure of the high-temperature modification of bismuth oxomolybdate γ-Bi_2MoO_6 tentatively determined on the basis of high-resolution electron microscopy data.[213] The difference between the *C*10 and *C*11 chains is reflected in the configurational and topological properties of the tetrahedra constituting

them. There are three configurational types of tetrahedra in the *C*10 polyion, each of which constitutes a topological equivalence class. The *C*11 chain consists of tetrahedra with five different configurations, two of which are of the same topological type. The example of these chains shows that the use of the configurational and topological properties of the tetrahedra is important for the classification of structural units.

***C*12**. The $\{uB, 1^1_\infty\}[O_2M_5]$ single chain (Fig. 7). In this chain, links *via* corners and edges alternate. An example of a compound with such a chain is provided by georgbokiite $Cu_5O_2(SeO_3)_2Cl_2$ (in the original study,[42] the coordination of the additional oxygen atom was not considered).

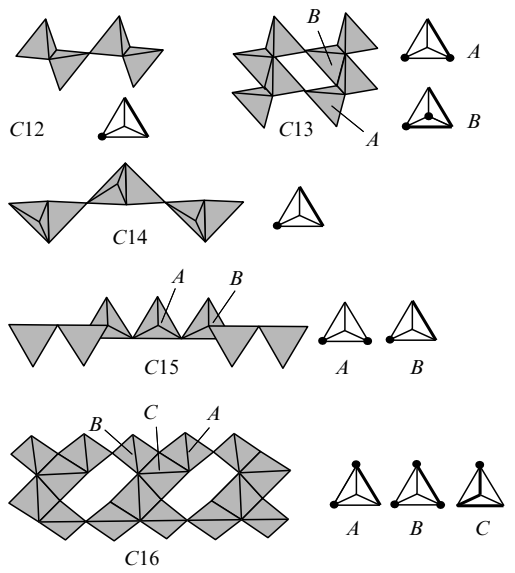


Figure 7. The types of oxocentred chain complexes (*C*12 – *C*16). *A*, *B*, *C* — tetrahedra belonging to different topological types.

***C*13**. The $\{uB, 2^1_\infty\}[OM_2]$ double chain, consisting of two type *C*12 chains, was first identified by Bergerhoff and Paeslack [19] in kyanite $Al_2O(SiO_4)$.[218]

***C*14**. The oxocentred $\{uB, 1^1_\infty\}[O_2M_5]$ chain, which may be found in compounds of the aenigmatite structural type, is a topological analogue of the *C*12 chain but with a periodicity of 4.[221–228]

***C*15**. The $\{uB, 1^1_\infty\}[O_6M_{16}]$ single chain with a periodicity of 6 is an interesting example of the alternation of two bonds *via* neighbouring corners with a single bond *via* the edge. This remarkable polyion, with the formula $[O_3Pb_8]$, may be identified in the structure of freedite $Pb_8Cu(AsO_3)_2O_3Cl_5$, solved by Pertlik,[67] who did not, however, consider it within the framework of the approach which we are employing.

***C*16**. The $\{lB, 1^1_\infty\}[OM_2]$ loop-branched chain has been detected in the structure of copper titanium oxoborate $Cu_9Ti(B_20_5)_2(BO_3)_2O_6$. This consists of two types of *C*1 chains linked by two additional tetrahedra adjoining them *via* two edges each. It is essential to note that this compound contains also 'additional' oxygen atoms involved in nontetrahedral (ternary) coordination and copper atoms which do not enter into the complex under consideration. The *C*16 chain is the only example of a branched complex involving oxocentred chains.

4. Layered oxocentred complexes

A series of layers may be described as derivative of the type PbO tetrahedral layer. Carre *et al.*[20] suggested that certain chains based on the [OLa_4] tetrahedron be also considered in terms of this aspect. However, the above principle is subject to limitations, since there are many structural units which cannot be detected among derivatives of the PbO layer regardless of the way in which it is 'sliced'. We therefore use this approach only for certain layered structures. Tables 7 and 8 present the characteristics of the types of layered oxocentred complexes based on [OM_4] tetrahedra and the chemical compounds in the structures of which these complexes have been detected.

Table 7. Classification of the types of oxocentred layered complexes based on the [OM_4] tetrahedron.

Number	*ML*	*L*	*P*	*B*	*M*	O:T	*m*	*n*	*p*	Connectedness formula
*L*1	1	1	2	*uB*	1	2:5	1	1	1	(3: 1 – 3)
*L*2	1	1	2	*uB*	1	2:5	1	1	1	(3: 1 – 3)
*L*3	2	1, 2	1	*uB*	2	1:1	1	1	1	(9: 1 – 6; 2 – 3)
*L*4	2	1, 2	1	*uB*	4	4:3	2	2	*A*1	(13: 1 – 10; 2 – 3)
									*B*1	(18: 1 – 12; 2 – 6)
*L*5	1, 2	1, 2	2	*uB*	1	4:5	1	1	1	(7: 1 – 4; 2 – 3)
*L*6	1, 2	1, 2	2	*uB*	1	6:7	2	2	*A*1	(7: 1 – 4; 2 – 3)
									*B*1	(8: 1 – 4; 2 – 4)
*L*7	1, 2	1, 2	2	*uB*	1	8:9	2	2	*A*1	(7: 1 – 4; 2 – 3)
									*B*1	(8: 1 – 4; 2 – 4)
*L*8	1, 2	1, 2	4	*lB*	1	1:2	1	1	1	(5: 1 – 4; 2 – 1)
*L*9	1, 2	1, 2	4	*uB*	1	2:3	1	1	1	(5: 1 – 3; 2 – 2)
*L*10	1, 2	1, 2	2	*uB*	1	1:2	1	1	1	(3: 1 – 2; 2 – 1)
*L*11	1, 2	1, 2	2	*uB*	1	1:2	1	1	1	(6: 1 – 5; 2 – 1)
*L*12	2	1, 2	2	*uB*	1	1:1	1	1	1	(8: 1 – 4; 2 – 4)
*L*13	2	1, 2	4	*uB*	1	1:1	1	1	1	(8: 1 – 4; 2 – 4)
*L*14	2	1, 2	3	*lB*	1	4:5	1	1	1	(6: 1 – 3; 2 – 3)
*L*15	1, 2	1, 2	4	*lB*	1	3:5	2	2	*A*2	(4: 1 – 2; 2 – 2)
									*B*1	(5: 1 – 2; 2 – 3)
*L*16	2	1, 2	2	*lB*	1	9:14	6	4	*A*1	(4: 1 – 2; 2 – 2)
									*B*1	(4: 1 – 2; 2 – 2)
									*C*1	(5: 1 – 2; 2 – 3)
									*D*1	(5: 1 – 2; 2 – 3)
									*E*1	(5: 1 – 3; 2 – 2)
									*F*1	(6: 1 – 2; 2 – 4)
*L*17	2	1, 2	2	*lB*	1	7:8	5	3	*A*2	(7: 1 – 4; 2 – 3)
									*B*2	(7: 1 – 4; 2 – 3)
									*C*1	(6: 1 – 2; 2 – 4)
									*D*1	(7: 1 – 3; 2 – 4)
									*E*1	(7: 1 – 3; 2 – 4)
*L*18	1, 2	1, 2	2	*hB*	1	11:12	5	5	*A*2	(9: 1 – 4; 2 – 5)
									*B*4	(11: 1 – 8; 2 – 3)
									*C*1	(12: 1 – 8; 2 – 4)
									*D*2	(8: 1 – 8)
									*E*2	(9: 1 – 8; 2 – 1)
*L*19	1, 2	1, 2	2	*lB*	1	4:7	5	5	*A*1	(4; 1 – 2; 2 – 2)
									*B*1	(4: 1 – 2; 2 – 2)
									*C*1	(3: 1 – 1; 2 – 2)
									*D*1	(4: 1 – 3; 2 – 1)
									*E*1	(4: 1 – 2; 2 – 2)
*L*20	2	1, 2	2	*uB*	2	4:3	1	1	1	(15: 1 – 10; 2 – 5)

***L*1**. The $\{uB, 1^2_\infty\}[O_2M_5]$ layer (Fig. 8) can be regarded as made up of *C*5 single chains. In terms of its structure, it resembles the $[Si_2O_5]$ tetrahedral networks constituting (together with octahedral networks) the structures of layered silicates.[76] However, the topological structures of the layer considered and the silicate layer differ, since the unshared corners of neighbouring tetrahedra in the *L*1 layer are turned in opposite directions relative to the plane of the layer. The difference between the silicate tetrahedral network and the L_1 layer is analogous to the difference between the pyroxene chain and the *C*5 chain. The structural unit $[O_2Cu_5]$ of the *L*1 type has been detected in the crystal structure of averievite $[Cu_5O_2](VO_4)_2 \cdot MCl$ (M = K, Rb, Cs) (Fig. 9).[232, 233] In this structure, the oxocentred layers are located exactly one under the other, the [VO_4] groups are 'glued' to the

Table 8. Oxocentred [OM_4] layered complexes in the crystal structures of inorganic compounds.

Number	Type of complex	Chemical formula of complex	Chemical compound	Ref.
*L*1	$\{uB, 1^2_\infty\}[O_2M_5]$	$[O_2Cu_3Pb_2]$	$Pb_2Cu_3O_2(NO_3)_2(SeO_3)_2$	231
		$[O_2Cu_5]$	$Cu_5O_2(VO_4)_2 \cdot MCl$ (M = K, Rb, Cs) (averievite)	232, 233
*L*2	$\{uB, 1^2_\infty\}[O_2M_5]$	$[O_2Cu_5]$	$NaCu_5O_3(SeO_3)_2Cl_3$	234
*L*3	$\{uB, 2^2_\infty\}[OM]$	[OX] (X = La, Ce, Pu)	La_2O_2S, Ce_2O_2S, Pu_2O_2S	235
			La_2O_2Se	236
			LaOF	237
*L*4	$\{uB, 1^2_\infty\}[O_4M_3]$	$[O_4(Bi,Sr)_3]$	$Bi_{0.765}Sr_{0.235}O_{1.383}$	238
*L*5	$\{uB, 1^2_\infty\}[O_4M_5]$	$[O_4Cu_3Bi_2]$	$Na_2[(Bi_2Cu_3O_4(AsO_4)_2] \cdot H_2O$	239
			$K_2[Bi_2Cu_3O_4(AsO_4)_2] \cdot 2H_2O$	239
*L*6	$\{uB, 1^2_\infty\}[O_6M_7]$	$[O_6Cu_3Bi_4]$	$Cu_3Bi_4V_2O_{14}$	240
*L*7	$\{uB, 1^2_\infty\}[O_8M_9]$	$[O_8Bi_9]$	$Bi_{20}O_{27}(SO_4)_{12}$	212
*L*8	$\{uB, 1^2_\infty\}[OM_2]$	$[OY_2]$	Y_2OS_2	241
*L*9	$\{uB, 1^2_\infty\}[O_2M_3]$	$[O_2Ce_2Cr]$	$(Ce_2CrO_2)CrS_4$	242
		$[O_2HgPb_2]$	$HgPb_2O_2Cl_2$	243
*L*10	$\{uB, 1^2_\infty\}[OM_2]$	$[OCu_2]$	$Cu_2O(SO_4)$ (dolerophanite)	23, 24
		$[O_2Cu_3Bi]$	$Cu_3Bi(SeO_3)_2O_2Cl$ (francisite)	244
*L*11	$\{uB, 1^2_\infty\}[OM_3]$	$[O(Mg,Mn)_2]$	$(Mg,Mn)_2Mn(BO_3)_2$	142, 245
		$[(O,F)_4(Ca,Na)_6ZrTi]$	$Ca_{3.5}Na_{2.5}Zr(Ti,Mn,Nb)(Si_2O_7)_2 \cdot F_2O(F,O)$ (rosenbuschite)	246
		$[(O,F)_2(Na,Ca,Ce)_3Ti]$	$(Na,Ca,Ce)_3Ti(Se_2O_7)(O,F)_2$ (mosandrite)	247
		$[(O,F)_2(Na,Ca)_2(Zr,Ti,Mn)_2]$	$(Na,Ca)_2(Zr,Ti,Mn)_2(Si_2O_7)(O,F)_2$ (seidozerite)	248, 249
		$[O_4Ti_3CaBa_4]$	$Na_2Ba_3(Ba,K,Mn)(Ca,Na)Ti(TiO_2)_2[Si_2O_7]_2(SO_4)_2$ (innelite)	250
		$[(O,F)_4(Ti,Al)_2(Ca,Na)_6]$	$(Ca,Na)_7(Ti,Al)_2(Si_2O_7)_2O(O,F)_3$ (goetzenite)	251
*L*12	$\{uB, 1^2_\infty\}[OM]$	[OPb]	PbO, *P*4/*nmm*	252
			PbO, *Cmma*	252
			$Pb_7O_8Cl_2$ (asisite)	253
		[OFe]	FeO(OH) (lepidocrocite)	254
		[OAl]	AlO(OH) (boehmite)	255
		$[O_3Bi_2Co]$	$Bi_2CoO_3SO_4$	256
		$[O_2PbBi]$	$PbBiO_2Cl$ (perite)	257, 258
		$[O_2PbSb]$	$PbSbO_2Cl$ (nadorite)	259
		[OM] (M = Bi, Nd, Gd, Dy)	(MO)(CuSe) (M = Bi, Nd, Gd, Dy)	260
		$[(O,OH)_4Pb_3(Sb,As)]$	$Pb_3Sb_{0.6}As_{0.4}(O_3OH)Cl_2$ (thorikosite)	261
		$[(O,OH)_2Pb_2]$	$Pb_2(O,OH)_2Cl$ (blixite)	261
		[OBi]	$Bi_2O_2(CO_3)$ (bismutite)	262
			$CaBi_2O_2(CO_3)_2$ (bayerite)	262
			BiOF (zavaritskite)	263, 264
			BiOCl (bismoclite)	265
			$Bi_2O_2(MoO_4)$ (koehlinite)	266–268
			$Bi_2O_2(WO_4)$ (russellite)	269
			$CaBiOF(CO_3)$ (kettnerite)	270
*L*13	$\{uB, 1^2_\infty\}[OM]$	[OPb]	PbO, *Pbcm*	271
*L*14	$\{lB, 1^2_\infty\}[O_4M_5]$	$[O_4Pb_4Ag]$	$AgPb_4O_4Cl$	272
*L*15	$\{lB, 1^2_\infty\}[O_3M_5]$	$[O_3Pb_5]$	$Pb_5O_3(GeO_4)$	61
*L*16	$\{lB, 1^2_\infty\}[O_9M_{14}]$	$[O_9Pb_{14}]$	$Pb_{14}(VO_4)_2O_9Cl_4$ (kombatite)	62, 63
			$Pb_{14}(AsO_4)_2O_9Cl_4$ (salinite)	273
*L*17	$\{lB, 1^2_\infty\}[O_7M_8]$	$[O_7Pb_8]$	$Ag_2Pb_8O_7Cl_4$	274
*L*18	$\{hB, 1^2_\infty\}[O_{11}M_{12}]$	$[O_8F_3(Ca,Na)_8(Ti,Nb)_4]$	$(Ca,Na)_8(Ti,Nb)_4(Si_2O_7)_2O_8F_3$ (fersmanite)	275
*L*19	$\{lB, 1^2_\infty\}[O_4M_7]$	$[O_4Pb_7]$	$Pb_{11}Si_3O_{17}$	155
			$Pb_{11}Ge_3O_{17}$	156
*L*20	$\{uB, 2^2_\infty\}[O_4M_3]$	$[O_4Ba_2Bi]$	$BaBi_4O_4I_2$	276

bases of the [OCu_4] tetrahedra and together with the layers form the fundamental electrically neutral $Cu_5O_2(VO_4)_2$ framework. As a consequence of the disposition of the layers one under the other, broad cavities with a radius in excess of 3.0 Å, which incorporate the alkali metal ions K^+, Rb^+, and Cs^+ as well as the chloride ions Cl^-, are formed in the structure.

L2. A layer of this type is a 'corrugated' analogue of the *L*1 layer. It is distorted in such a way that the periodicity of the fundamental chain of the layer changes from 2 to 3. This layer has been detected by Shuvalov *et al.*[234] in the crystal structure of $NaCu_5O_2(SeO_3)_2Cl_3$.

L3. The oxocentred $\{uB, 2^2_\infty\}$[OM] layer with the chemical formula [OLa] was identified by Bergerhoff and Paeslack [19] in the La_2O_2S structure solved by Zachariasen.[235] The multiplicity of this layer is 2, although it can be regarded as consisting of two corner-linked layers with a periodicity of 1.

L4. The [O_4M_3] structural unit of this type consists of two *L*3 layers 'glued' to one another or of four simple corner-linked single-period layers. As a result of the 'glueing', the O : M ratio becomes 1.333, *i.e.* greater than 1.

L5, ***L6***, ***L7***. The layers of these types can be regarded as a result of the successive linking of *C*7 chains. The *C*7 chains are initially linked *via* their edges into multiple chains similar to *C*8 and *C*9,

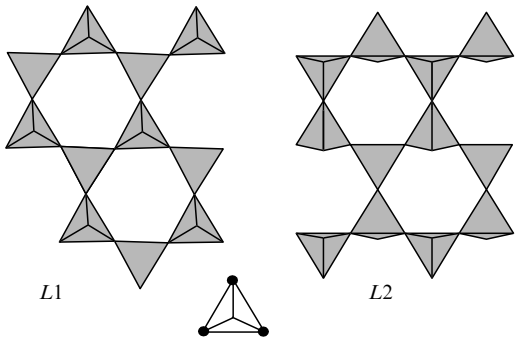


Figure 8. The types of oxocentred layered complexes *L*1 and *L*2.

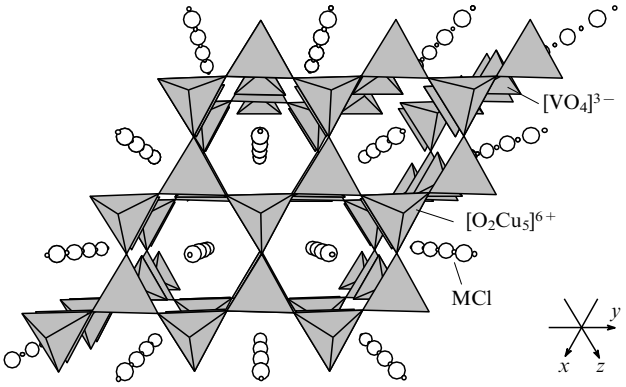


Figure 9. The crystal structure of averievite $Cu_5O_2(VO_4) \cdot MCl$.

after which these multiple chains are linked *via* lateral corners into infinite layers. Thus the *L*5 and *L*6 layers can be regarded as consisting of *C*8 and C9 chains respectively. The *L*7 layer is formed from a *C*7 four-fold chain, the individual fragments of which have not so far been detected in chemical compounds. The possibility of identifying the *L*7 layer in the $Bi_{26}O_{27}(SO_4)_{12}$ crystal structure has been pointed out.[212] The *L*5 and *L*6 layers were not considered in the original studies. It is of interest that the last two layers in compounds have similar chemical compositions — $[O_4Cu_3Bi_2]$ and $[O_6Cu_3Bi_4]$ respectively. In these complexes, the Bi atoms participate only in the edge-linking of the *C*7 chains into multiple chains, whereas the Cu atoms are involved in corner-linking into a layer of the multiple fragments formed. Thus the functions of the cations in the topological structures of the *L*5 and *L*6 layers are different.

***L*8**. The $\{uB, 1^2_\infty\}[OM_2]$ layer may be regarded as consisting of finite *I*4 complexes.

***L*9**. A type *L*9 layer was first described by Keller and Langer [243] in the structure of $HgPb_2O_2Cl_2$. The layer is made up of *C*3 chains by the linking of the latter *via* the corners of the tetrahedra not involved in edge-linking.

***L*10**. A $\{uB, 1^2_\infty\}[OM_2]$ layer has been noted by Bergerhoff and Paeslack [19] in the crystal structure of dolerophanite $Cu_2O(SO_4)$. This layer can also be identified in the structure of francisite [244] (Pring *et al.*[244] did not consider the structure of the oxocentred layer).

***L*11**. A type *L*11 layer may be found in the crystal structure of pinakiolite $(Mg, Mn)_2Mn^{3+}(BO_3)O_2$. Together with the tetrahedrally coordinated 'additional' oxygen atoms, pinakiolite contains 'additional' oxygen atoms with the [4 + 1] coordination — a 'tetragonal pyramid' — as well as metal atoms not involved in the oxocentred groups. On the other hand, all the 'additional' oxygen atoms in the structures of a series of diorthosilicates belonging to the mosandrite–rosenbuschite group [246–251] are involved in tetrahedral coordination, while all the cations (with the exception of innelite and goetzenite) participate in the formation of the oxocentred tetrahedra. As in the case of the structures of the cuspidine series (with a *C*3 chain), the central oxygen atom in the [OM_4] tetrahedra is partly substituted by fluorine, which does not disturb the overall structure of the complex.

***L*12**. The [OM] layer. The [OM] layer is one of the commonest layers with edge-linking of tetrahedral complexes. For example, in the case of lead monoxide [tetragonal and one of the orthorhombic (*Cmma*) modifications], the [OPb] layer is made up of [OPb_4] tetrahedra.[252] An oxocentred layer of this type has been detected in the structures of a multiplicity of chemical compounds (see a review [277] as well as Table 8).

***L*13**. The layer in the orthorhombic (*Pbcm*) PbO [271] differs structurally from *L*12 by the marked 'corrugations' of the PbO layers. The topological structures of these layers are also different, although their constituent [OPb_4] tetrahedra are topologically equivalent.

***L*14**, ***L*15** (Fig. 10), ***L*16**. These layers can be readily obtained by 'cutting out' different blocks of OPb_4 tetrahedra from the tetragonal PbO layer. In $AgPb_4O_4Cl$,[272] one tetrahedron is 'cut out' in each case, whereas in $Pb_5O_3(GeO_4)$[61] blocks of six tetrahedra (three by two in size) are 'cut out'. In the kombatite [62, 63] and sahlinite [273] structures, 'butterflies' consisting of seven [OPb_4] tetrahedra are 'cut out'. In the layers formed after 'cutting out', the symmetry of the [OPb_4] is distorted as a consequence of the removal of neighbouring tetrahedra.

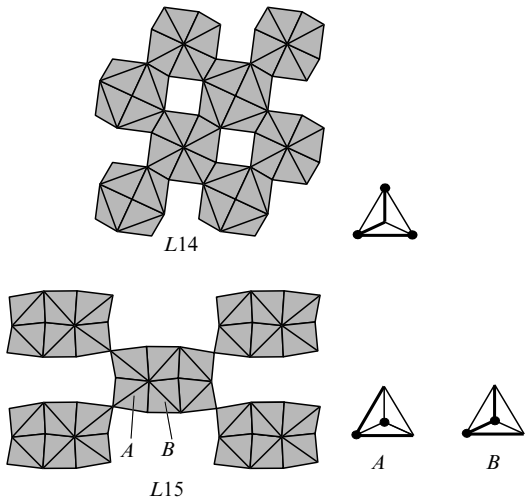


Figure 10. The oxocentred layered complexes *L*14 and *L*15.

***L*17**. The [O_7Pb_8] layer of this type is a highly 'corrugated' version of the *L*12 and *L*13 layers, where individual [OPb_4] tetrahedra have been 'cut out'. The O : M ratio in such a layer is 7 : 8.

***L*18**. The oxofluorocentred $[O_8F_3(Ca, Na)_8(Ti, Nb)_4]$ layer, made up of a defective (with one-tetrahedron 'cut out') *L*12 layer to which single type *C*1 chains have been added from above and from below, may be identified in the crystal structure of the mineral fersmanite.[275] The addition takes place in such a way that the direction of the *C*1 chain from the upper side of the layer is perpendicular to the direction of the same chain from the lower side. Each second tetrahedron of the chain is then located above or below the 'cut out' in the main layer. The [Si_2O_7] diorthosilicate groups are located between the layers having this structure in fersmanite. In the original study,[275] the oxocentred complexes were not identified.

***L*19**. A layer of this type is made up of three-period chains with alternation: two linkages *via* the edges and one linkage *via* a corner. Such chains are loop-branched, since they are connected by two additional tetrahedra.

***L*20**. The $[O_4M_3]$ double layer is made up of two *L*12 layers edge-linked to one another.

5. Oxocentred framework complexes

The classification of three-dimensional polyhedral structures is one of the important problems in the crystal chemistry of inorganic compounds. Tables 9 and 10 present the types of oxocentred framework complexes based on $[OM_4]$ tetrahedra and the chemical compounds containing them.

Table 9. Statistics of oxocentred framework complexes based on $[OM_4]$ tetrahedra.

Number	*ML*	*L*	*P*	*B*	O : T	*m*	*n*	*p*	Connectedness formula
*F*1	1	1	2	*uB*	1 : 2	1	1	1	(4: 1 – 4)
*F*2	1	1	2	*uB*	1 : 2	1	1	1	(4: 1 – 4)
*F*3	1	1	1	*uB*	1 : 1	1	1	1	(12: 1 – 12)
*F*4	1	1	1	*lB*	6 : 11	2	1	*A*1	(5: 1 – 5)
								*B*2	(5: 1 – 5)
*F*5	1, 2	1, 2	2	*uB*	1 : 1	1	1	1	(10: 1 – 8; 2 – 2)
*F*6	1, 2	1, 2	4	*lB*	2 : 3	1	1	1	(6: 1 – 5; 2 – 1)
*F*7	1, 2	1, 2	1	*uB*	1 : 1	1	1	1	(13: 1 – 10; 2 – 3)
*F*8	1, 2	1, 2	2	*uB*	2 : 3	1	1	1	(7: 1 – 6; 2 – 1)
*F*9	1, 2	1, 2	1	*uB*	1 : 1	3	2	*A*1	(8: 1 – 4; 2 – 4)
								*B*1	(8: 1 – 4; 2 – 4)
								*C*1	(10: 1 – 8; 2 – 2)
*F*10	2	1, 2	2	*uB*	2 : 1	1	1	1	(22: 1 – 16; 2 – 6)
*F*11	2	1, 2	2	*lB*	3 : 2	1	1	1	(16: 1 – 12; 2 – 4)
*F*12	2	1, 2	5	*lB*	1 ; 1	1	1	1	(9: 1 – 6; 2 – 3)
*F*13	1, 2	1, 2	4	*lB*	2 : 3	1	1	1	(4: 1 – 1; 2 – 3)
*F*14	1, 2	1, 2	4	*uB*	2 : 3	2	2	*A*1	(8: 1 – 7; 2 – 1)
								*B*1	(6: 1 – 6)
*F*15	1, 2	1, 2	2	*uB*	3 : 2	1	1	1	(16: 1 – 12; 2 – 4)
*F*16	1, 2	1, 2	2	*uB*	2 : 3	1	1	1	(7: 1 – 6; 2 – 1)
*F*17	1, 2	1, 2	2	*hB*	3 : 4	3	3	*A*1	(8: 1 – 7; 2-1)
								*B*1	(10: 1 – 9; 2 – 1)
								*C*1	(10; 1 – 10
*F*18	1, 2	1, 2	2	*uB*	2 : 3	4	2	*A*1	(9: 1 – 8; 2 – 1)
								*B*1	(8: 1 – 8)
								*C*1	(8: 1 – 8)
								*D*1	(8: 1 – 8)
*F*19	1, 2	1, 2	2	*uB*	6 : 7	1	1	1	(15: 1 – 14; 2 – 1)
*F*20	1, 2	1, 2	2	*oB*	9 : 14	2	2	*A*1	(10: 1 – 8; 2 – 2)
								*B*2	(7: 1 – 6; 2 – 1)
*F*21	1, 2	1, 2	3	*lB*	10 : 13	5	5	*A*1	(4: 1 – 2; 2 – 2)
								*B*1	(5: 1-2; 2 – 3)
								*C*1	(6: 1 – 3; 2 – 3)
								*D*1	(7: 1 – 3; 2 – 4)
								*E*1	(8: 1 – 4; 2 – 4)

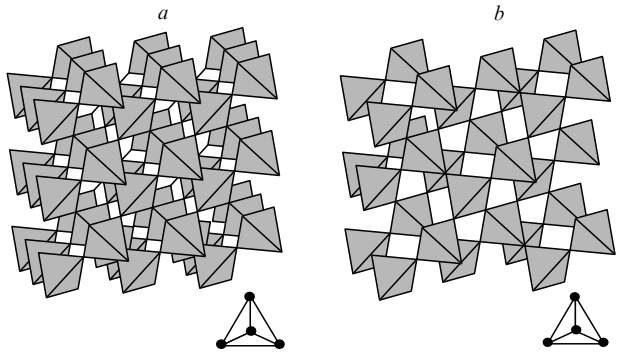


Figure 11. The crystal structure of cuprite Cu_2O and the $[OCu_2]$ double framework made up of $[OCu_4]$ tetrahedra (*a*) and the *F*1 framework (*b*).

Table 10. Chemical compounds containing oxocentred framework complexes based on $[OM_4]$ tetrahedra.

Number	Type of complex	Chemical formula of complex	Chemical compound	Ref.
*F*1	$\{uB, {}^3_\infty\}[OM_2]$	$[OCu_2]$	Cu_2O (cuprite)	278
		$[OCu_2]$	Cu_2OCl_2 (melanothallite)	279
			$Cu_2O(SeO_3)$, $P2_1/n$	51
			$Cu_2O(SeO_3)$, $P2_13$	51
		$[OPb_2]$	Pb_2O	280
			Pb_2OF_2	281
		$[OPd_2]$	Pd_2OCl_2	282
		$[OFe_2]$	β-$Fe_2O(PO_4)$	283, 284
		[ONiCr]	$NiCrO(PO_4)$	283
		$[OA_2]$ (A = Hg, Cd, Ag, Bi, Pb *etc*.)	$A_2(B_2O_6)O$ (B = Ru, Rh, Ti, Cr *etc*.) (pyrochlores)	285, 286, 287
*F*2	$\{uB, {}^3_\infty\}[OM_2]$	$[O_2MgAl_3]$	$MgAl_3O_2(SiO_4)(BO_3)$	288
*F*3	$\{uB, {}^3_\infty\}[OM]$	[OZn]	ZnO (zincite)	289, 290
		[OBe]	BeO (bromellite)	291
*F*4	$\{lB, {}^3_\infty\}[O_6M_{11}]$	$[O_{12}Bi_4Ag_{18}]$	$Bi_4Ag_{18}O_{12}$	292
*F*5	$\{uB, {}^3_\infty\}[OM]$	[OCu]	CuO (tenorite)	293
			AgO	293
*F*6	$\{lB, {}^3_\infty\}[O_2M_3]$	$[O_2Cd_3]$	$Cd_3O_2Cl_2$	294
*F*7	$\{uB, {}^3_\infty\}[OM]$	$[O_2CuFe]$	$CuFeO_2$ (delafossite)	295, 296
		$[O_2AgFe]$	$AgFeO_2$	297
		$[O_2CuM]$ (M = Al, GaSc, Y)	$CuMO_2$ (M = Al, GaSc, Y)	298
*F*7	$\{uB, {}^3_\infty\}[OM]$		$CuAlO_2$	299
		$[O_2CuMn]$	$CuMnO_2$ (crednerite)	300
*F*8	$\{uB, {}^3_\infty\}[O_2M_3]$	$[O_4Cu_5Sn]$	$Cu_5Sn(BO_3)_2O_4$	301
*F*9	$\{uB, {}^3_\infty\}[OM]$	[(F,O)Pb]	$Pb_{12}Ta_9O_{20}F_{29}$	302
*F*10	$\{uB, {}^3_\infty\}[O_2M]$	$[O_2Ce]$	CeO_2	303
*F*11	$\{lB, {}^3_\infty\}[O_3M_2]$	$[O_3FeMn]$	$FeMnO_3$	304
		$[O_3CuTi]$	$Cu_{1-x}Ti_{1-x}Fe_{2x}O_3$	305
*F*12	$\{lB, {}^3_\infty\}[OM]$	[OIn]	$In_6O_6(WO_6)$	306
*F*13	$\{lB, {}^3_\infty\}[O_2M_3]$	$[O_2La_3]$	$La_3Ir_3O_{11}$	307
		$[O_2Bi_3]$	$Bi_3Ru_3O_{11}$	308, 309
*F*14	$\{uB, {}^3_\infty\}[O_2M_3]$	$[O_2Co_{2.1}Al_{0.9}]$	$Co_{2.1}Al_{0.9}BO_5$	310
		$[O_2Ni_2Al]$	Ni_2AlBO_5	310
		$[O_2Cu_2Al]$	Cu_2AlBO_5	310
*F*15	$\{uB, {}^3_\infty\}[O_3M_2]$	$[O_3Al_2]$	Al_2O_3 (corundum)	311
*F*16	$\{uB, {}^3_\infty\}[O_2M_3]$	$[O_2Ag_2Pb]$	Ag_2PbO_2	312, 313
		$[O_2Cu_2Pb]$	$PbCu_2O_2$	314
*F*17	$\{hB, {}^3_\infty\}[O_3M_4]$	$[O_3Ag_3Bi]$	Ag_3BiO_3	315
*F*18	$\{uB, {}^3_\infty\}[O_2M_3]$	$[O_4Ag_5Bi]$	Ag_5BiO_4	315
*F*19	$\{uB, {}^3_\infty\}[O_6M_7]$	$[O_6Ag_5Pb_2]$	$Ag_5Pb_2O_6$	312
*F*20	$\{uB, {}^3_\infty\}[O_9M_4]$	$[O_{18}Ag_{25}Bi_3]$	$Ag_{25}Bi_3O_{18}$	316
*F*21	$\{lB, {}^3_\infty\}[O_{10}M_{13}]$	$[O_{10}Pb_{13}]$	$Pb_{13}O_{10}Br_6$	317

***F*1** (Fig .11). The oxocentred type *F*1 framework is a reverse analogue of the cristobalite framework, which has been frequently noted by many investigators (see, for example, Belov [77]). The crystal structure of cuprite Cu_2O [277, 278] consists of two interpenetrating electrically neutral anticristobalite $[OCu_2]$ frameworks (Fig. 11*a*). When univalent copper is replaced by divalent copper, the $[OCu_2]$ framework (Fig. 11*b*) acquires a 2+ charge per tetrahedron. The introduction of additional anions into this framework in order to compensate for the charge leads to the

crystal structures of melanothallite Cu_2OCl_2 [279] and $Cu_2O(SeO_3)_2$ (two modifications [51]). Similar frameworks with additional anions occur also in the Pd_2OCl_2 [282] and Pb_2OF_2 [281] structures. The latter structure was examined by Bergerhoff and Paeslack [19] as an oxocentred framework. Pannetier and Lucas [286] suggested that the $A_2B_2O_6O'$ pyrochlore structural type, in particular, be considered as one containing the cuprite-like A_2O' (A = Sc, Y, Ln, Bi, Cd, Hg, Pb, *etc*.) framework. The following considerations were adduced in support of this model: firstly, the model makes it possible to consider the characteristic features of the disposition of the O′ atom (position 8*b*), the orbitals of which are sp^3-hybridised and the coordination is represented by a regular tetrahedron; secondly, the distortion of the cubic pyrochlore structure may be compared with the observed distortions of the polymorphic modifications of silica SiO_2; thirdly, if position *A* is occupied by a d^{10} atom of type Hg^{2+}, Cd^{2+}, or Ag^+, the A–O′ bond becomes stronger than the A–O bond and the O′ oxygen becomes less mobile. The possibility of describing the pyrochlore structure taking into account the tetrahedral coordination of the O′ oxygen has also been pointed out by Belov *et al*.[287]

***F*2**. The oxocentred [O_2MgAl_3] framework, made up of *L*1 layers linked *via* corners not participating in the formation of the layer, may be identified in the crystal structure of grandidierite.[288]

***F*3**. The *F*3 framework is the oxocentred version of the wurtzite structure. Four [OZn_4] tetrahedra converge at each corner of this framework.

***F*4**. The oxocentred [O_6M_{11}] framework has been found in the $Bi_4Ag_{18}O_{12}$ structure.[292] This framework consists of two types of fundamental chains — two-period *C*5 chain and a four-period chain formed as a result of the corner-linking of tetrahedra. In the structure of this compound, the chains are parallel to the *y* axis. This structure shows that the topological equivalence of all the tetrahedra in the polyion does not as yet ensure their configurational equivalence. In this structure, there are two configurational types of tetrahedra belonging to one topological class.

***F*5**. The oxocentred framework of this type is made up of *C*7 lanarkite chains linked by the corners of the tetrahedra so that four tetrahedra converge at a single corner.

***F*6**. The *F*6 framework is made up of *L*8 layers linked by nonshared corners of the tetrahedra.

***F*7**. The delafossite $CuFeO_2$ structural type consists of a framework made up of continuous hexagonal layers of [$OCuFe_3$] tetrahedra linked *via* corners at which the copper atoms are located; within the layer, the linking is *via* the iron atoms.[295, 296]

***F*8**. The [O_2M_3] framework may be represented as consisting of single type *C*12 chains.

***F*9**. The type *F*9 framework is made up of *C*1 chains linked in the following way: six *C*1 chains fitted together edgewise form a six-fold chain belonging to the O_nM_{n+2} family. The complex chains linked in this way are linked *via* the corners of the tetrahedra to form a framework dividing space into a series of broad parallel channels with a square cross-section. In the crystal structure of the compound $Pb_{12}Ta_9O_{20}F_{29}$, infinite columns of [TaO_6] octahedra are accommodated in these channels.[302]

***F*10**, ***F*11**, ***F*12**. The frameworks of these types may be regarded as derivatives of the fluorite CaF_2 structure, which can be represented in its turn as one consisting of [FCa_4] tetrahedra. CeO_2,[303] the structure of which is made up of [OCe_4] tetrahedra, is an analogue of fluorite. The structural type of bixbyite [304, 305] corresponds to a defective fluorite framework, like the [OIn] framework in the crystal structure of $In_6O_6(WO_6)$.[306]

***F*13** (Fig. 12*a*). The *F*13 type framework is made up of finite groups *I*6 linked by nonshared corners. The $La_3Ir_3O_{11}$ structure [307] includes two interpenetrating [O_2La_3] frameworks.

***F*14** (Fig. 12*b*). The three-dimensional [O_2M_3] structure, characteristic of the crystal structures of aluminoborates M_2AlBO_5 (M = Co, Cu, Ni), has one-dimensional distorted hexagonal cavities in which the (BO_3) anions are accommodated.[310]

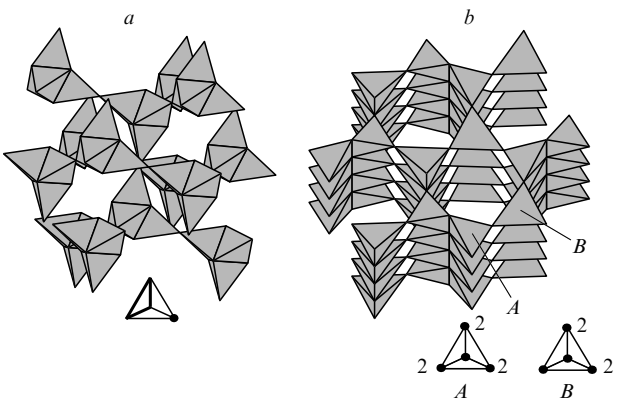


Figure 12. The oxocentred frameworks *F*13 (*a*) and *F*14 (*b*).

***F*15**. The type *F*15 framework describes the crystal structure of corundum Al_2O_3 when it is considered taking into account the tetrahedral coordination of the oxygen atoms.[311] It is possible to describe the structure as hexagonal close packing of the oxygen atoms in which octahedral cavities are filled by aluminium atoms. However, the latter are appreciably displaced from the centres of the octahedral cavities, which is due to the tendency of oxygen to acquire the ideal tetrahedral coordination. The structure of corundum is also remarkable because three [OAl_4] tetrahedra are linked together in it *via* a single [Al–Al] edge.

***F*16**. The [O_2M_3] framework consists of *C*12 single chains linked *via* corners participating in edge-linking within the chain.

***F*17**. Analysis of the Ag_3BiO_4 structure showed that it contains a complex oxocentred framework made up of [OAg_3Bi] tetrahedra of three configurational types.[315]

***F*18**. In the crystal structure of Ag_5BiO_4, there is a complex framework with the ratio O : M = 2 : 3.[315] This framework is formed as a result of the intertwining of *C*5 single chains, so that five-petal 'flowers' made up of oxocentred tetrahedra converging at one corner are produced.

***F*19**. The *C*12 chains in the $Ag_5Pb_2O_6$ structure are joined together in threes to form columns with a trigonal symmetry and are linked into a framework *via* the corners of the tetrahedra not participating in the linking process.[312]

***F*20**. In the study of the crystal structure of $Ag_{25}Bi_3O_{18}$ [316] within the framework of the approach employed, a single common edge [Bi–Ag] between three [OAg_3Bi] tetrahedra was noted. This framework consists of [OAg_3Bi] tetrahedra of two topological types. The type *A* tetrahedra, linked to form triple edge 'knots', consist of vertical columns with symmetry 3. The type *B* tetrahedra form groups made up of six tetrahedra converging at one corner. These groups link the vertical 'knotted' columns into a three-dimensional framework.

***F*21**. The *F*21 framework was identified by Riebe and Keller [317] in the crystal structure of $Pb_{13}O_{10}Br_6$. It consists of infinite chains of corner-linked [OPb_4] tetrahedra. These complex chains, arranged crosswise in the structure, are linked *via* the corners of the tetrahedra into a three-dimensional framework.

6. Structures with different oxocentred complexes

In conclusion of the description of the topological types of oxocentred complexes, it is essential to note the existence of the structural type with two different complexes based on [OM_4] tetrahedra. In the crystal structures of the compounds $Pb_{11}Si_3O_{17}$ [155] (Fig. 13), and $Pb_{11}Ge_3O_{17}$,[156] there are two oxocentred polyions of different dimensionality — the *C*3 chain and the *L*19 layer. The [OPb_2] *C*3 chains are arranged in the (001) plane in the form of a layer (without mutual linking), while the [O_4Pb_7] *L*19 layer is parallel to this plane. These layers alternate, the orthosilicate and diorthosilicate groups $[SiO_4]^{4-}$ and $[Si_2O_7]^{6-}$ being located in the space between them. The crystal-

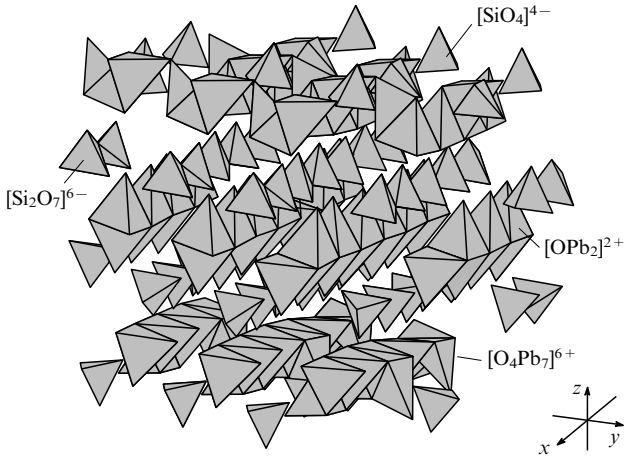


Figure 13. The crystal structure of $Pb_{11}Si_3O_{17}$.

chemical formula of the $Pb_{11}Si_3O_{17}$ structure should be written thus:

$$\{IB, 1^2_\infty\}[O_4Pb_7](\{uB, 1^1_\infty\}[OPb_2])_2[SiO_4]\{f\}[Si_2O_7].$$

The presence in this structure of different polycations and polyanions can be accounted for by their mutual stabilisation. The presence of silicate anions of two types and of different oxocentred structural units weakens the stresses generated.

V. Statistics of the corner and edge-linking [OM_4] tetrahedra

The ability of oxocentred tetrahedra to be linked together in two different ways (*via* corners and edges) has led to the statistical analysis of different types of linking among the 63 polyions described.

We shall define the sharing index of an element of the tetrahedral group (corner, edge) as the number of tetrahedra between which the element is shared regardless of the method of sharing. The average sharing index of the corners of the tetrahedron v will be defined as the average of the sharing indices of its corners. Thus, if v_1, v_2, v_3, and v_4 are the indices of the corners of the tetrahedron, it follows that

$$v = \frac{\sum v_i}{4}, \quad i = 1-4\,.$$

By analogy with v, we shall define the average sharing index of the edges of the tetrahedron e:

$$e = \frac{\sum e_i}{6}, \quad i = 1-6\,,$$

where e_i is the sharing index of the ith edge in the tetrahedron.

The average sharing index of an element [a corner ($\bar{v}$) or an edge ($\bar{e}$)] in the complex will be defined as the arithmetical mean of the sharing indices of the elements of topologically different tetrahedra. Account is taken of the number of tetrahedra of the given topological type in the complex. Thus, if there are two topological types of tetrahedra, A and B, in the complex in proportions of 2 : 1, then the average sharing index of the corners in the polyion is calculated by the formula

$$\bar{v} = \frac{2v_A + v_B}{3},$$

where v_A and v_B are the average sharing indices of the corners in the tetrahedra A and B.

The average sharing indices of the corners and edges in oxocentred complexes are presented in Table 11. For each dimensionality, the values have been averaged with respect to the number of polyions. It was found that the values of $\bar{v}$ naturally increase on passing from finite to framework complexes: 1.604 for I, 2.437 for C, 3.376 for L, and 3.886 for F (Fig. 14) As regards edge-linking, the values of $\bar{e}$ increase from 1.153 to 1.427 (1.278 for chains) on passing from finite layered complexes, but in the case of frameworks $\bar{e}$ diminishes to 1.328. This shows that edge-linking is most favourable for the linking of the [OM_4] tetrahedra into a layer, *i.e.* into a two-dimensional structure. For framework complexes, this type of linking is less common apparently because the involvement of a large number of edges in a tetrahedral structure leads to an unduly high concentration of oxygen atoms and a decrease in the stability of the complex. The frameworks are formed preferentially by the corner-linking of the tetrahedra.

The average sharing indices of the corners and edges for oxocentred complexes as a whole, calculated from the data

Table 11. The average connectedness indices of the corner ($\bar{v}$) and the edge ($\bar{e}$) in oxocentred complexes.

Number	$\bar{v}$	$\bar{e}$	Number	$\bar{v}$	$\bar{e}$	Number	$\bar{v}$	$\bar{e}$
*I*1	1	1	*L*1	1.750	1	*F*1	2	1
*I*2	1.25	1	*L*2	1.750	1	*F*2	2	1
*I*3	1.375	1	*L*3	4	1.500	*F*3	4	1
*I*4	1.50	1.167	*L*4	6	1.750	*F*4	2.250	1
*I*5	2	1.250	*L*5	3.500	1.500	*F*5	4	1.333
*I*6	2.500	1.500	*L*6	3.667	1.556	*F*6	2.750	1.167
	1.604 [a]	1.153 [a]	*L*7	3.750	1.583	*F*7	5	1.500
*C*1	1.500	1	*L*8	2.500	1.167	*F*8	3	1.167
*C*2	1.750	1	*L*9	2.750	1.333	*F*9	4	1.556
*C*3	2.500	1.333	*L*10	2	1.167	*F*10	8	2
*C*4	3	1.444	*L*11	2.750	1.167	*F*11	6	1.667
*C*5	1.500	1	*L*12	4	1.667	*F*12	4	1.500
*C*6	2.000	1.083	*L*13	4	1.667	*F*13	2.750	1.500
*C*7	2.000	1.333	*L*14	3.250	1.500	*F*14	2.875	1.083
*C*8	3	1.500	*L*15	2.667	1.389	*F*15	6	1.667
*C*9	3.333	1.556	*L*16	2.875	1.444	*F*16	3	1.167
*C*10	4.333	1.611	*L*17	3.571	1.619	*F*17	3.500	1.111
*C*11	4.333	1.611	*L*18	4.091	1.424	*F*18	3.125	1.042
*C*12	1.750	1.167	*L*19	2.450	1.267	*F*19	5	1.167
*C*13	2.250	1.250	*L*20	6	1.833	*F*20	5	1.222
*C*14	1.750	1.167		3.376 [a]	1.427 [a]	*F*21	3.350	1.533
*C*15	1.667	1.111					3.886 [a]	1.328 [a]
*C*16	2.33	1.278						
	2.437 [a]	1.278 [a]						

[a] Average value.

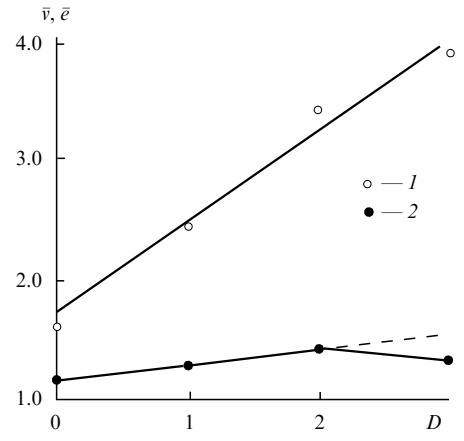


Figure 14. Dependence of the average sharing indices of the corners (*1*) and edges (*2*) on the dimensionality of the oxocentred complexes.

presented in Table 11, proved to be 3.139 and 1.330 respectively. Thus each corner in the oxocentred complexes based on the [OM_4] tetrahedra belongs on average to three tetrahedra and each edge belongs to $1\frac{1}{3}$ tetrahedra.

We may note that the edge-linking of tetrahedra inevitably increases the sharing index of their corners. Thus one (out of six) shared edge of the tetrahedra increases the average sharing index $\bar{e}$ by 1/6 and, by creating two (out of four) common corners, it increases $\bar{v}$ by 0.5. If the fraction due to edge-linking is subtracted from v, we obtain the following values of $\bar{v}$ for pure corner-linking: 1.145 for *I*, 1.603 for *C*, 2.098 for *L*, and 2.902 for *F*. This demonstrates yet again the importance of corner-linking in the organisation of oxocentred frameworks.

VI. Rules governing the linking of oxocentred [OM_4] tetrahedra

The description of the established types of cationic complexes based on oxocentred [OM_4] tetrahedra can be usefully completed by the rules according to which individual tetrahedra are linked together into a structural fragment.

1. The [OM_4] tetrahedra can be linked together *via* corners (M) and/or edges (MM).

2. One corner may be shared by more than two oxocentred tetrahedra but as a rule by not more than eight tetrahedra.

3. One edge is usually shared by not more than two oxocentred tetrahedra and in exceptional cases by three tetrahedra.

4. The corner-linking of the [OM_4] tetrahedra is characteristic of polyions of any dimensionality, while edge-linking is primarily characteristic of finite chain and layered structural units. The frameworks are formed mainly as a result of the corner-linking of tetrahedra.

The elucidation of the maximum number of tetrahedra converging at one corner constitutes an interesting problem. If the set of tetrahedra ('petals') converging at one corner is called a 'flower', then the maximum number of 'petals' (8) has been noted in topologically identical 'flowers' produced from the four-fold layer *L*4, the double layer *L*20, and the fluorite-like framework *F*10. The central atoms in these 'petals' are Bi, Ba, and Ce respectively. It was found that, among the oxocentred complexes known to us, there are eleven topologically different 'flowers' in which the number of 'petals' ranges from 5 upwards. Evidently the 'flower' with eight 'petals' constitutes the limit, the addition of yet another tetrahedron to the latter being impossible without the formation of a face-linkage.

The instance where three tetrahedra are edge-linked has not apparently been encountered in the crystal structures of anionic complexes with tetrahedral structural units, but does occur in the oxocentred corundum frameworks [O_3Al_2] and [$O_{18}Ag_{25}Bi_3$]. In the latter case, the steric interactions of the M corners not involved in the three-fold edge-linking of two neighbouring tetrahedra are weakened as a result of the inclination of the M – M edge relative to the horizontal. If one edge in the tetrahedral complexes may be shared by not more than three tetrahedra, then the distance *R* between nonshared M corners of neighbouring tetrahedra corresponds exactly to the length of the M – M edge. If four tetrahedra are linked *via* a single edge, (without a face-linkage), the distance *R* cannot be greater than or equal to the length of the M – M edge without complete loss of tetrahedral geometry by the linked complexes.

$Sn_2O(SO_4)$, $Pb_2O(SO_4)$ (lanarkite), and $Cu_2O(SO_4)$ (dolerophanite) may serve as examples of compounds in which the chemical composition of the cations influences the topology of the oxocentred polyion. In the first compound, there are finite groups *I*6 having the composition [O_4Sn_8], in lanarkite there are *C*7 [OPb_2] chains, whilst in dolerophanite there are *L*10 [OCu_2] layers.

Analysis of the incidence of various structural units based on [OM_4] tetrahedra shows that complexes made up of configurationally and topologically equivalent tetrahedra are commonest. This is fully consistent with Pauling's rule.

VII. Statistics of the M – O bond lengths and M – O – M bond angles in [OM_4] complexes

It was stated above that, as a consequence of the edge-linking of two tetrahedra, the value of the opposite bond angle diminishes. The average values of the M – O – M bond angles based on the M – M edge shared by two [OM_4] tetrahedra are listed in Table 12 for M = Cu, Sn, Pb, and La.‡ Evidently the M – O – M angle depends on the size of the atom M. The greater the M – O bond length, the smaller the diminution of the M – O – M angle. It is of interest that the average value < M – O – M > for all the atoms M considered is close to the 'ideal' value of 109.5°. The decrease in one or several M – O – M angles, induced by the presence of a common edge in the tetrahedron, is compensated by the increase in the bond angles based on the nonshared edges.

Table 12. The average M – O – M bond angles in [OM_4] complexes.

Bond	M – O /Å	M – O – M /deg [a]		M – O – M /deg [b]	
		I	II	I	II
Cu – O	1.94	93.5 (91.4 – 95.9)	12	109.6	72
Sn – O	2.26	101.8 (98.1 – 104.4)	3	109.0	6
Pb – O	2.33	103.1 (94.4, 98.2 – 109.2)	83	109.5	120
La – O	2.36	104.4 (101.6 – 107.6)	32	109.4	48
		average value		109.5	246

Note. The following designations have been adopted: I — average values of the angles, the limits of the variation of the angle in the structure being indicated in brackets; II — number of values taken into account.
[a] Values for the angle based on the common edge. [b] Values for all the angles in the tetrahedron.

Another fundamental feature of [OM_4] complexes is the possibility of the linking at one atom M of several [OM_4] tetrahedra. Table 13 presents the average M – O bond lengths for M corners of different connectedness in complexes with M = Cu or Pb. The M – O bond lengths for a nonshared M corner and for a M corner linking two [OM_4] tetrahedra do not actually differ. When the M – M edge is shared and the number of tetrahedra converging at an atom M increases, the M – O bond length also increases. When a corner is shared by three tetrahedra so that one tetrahedron is edge-linked to a second tetrahedron and corner-linked to a third tetrahedron (Table 13), the M – O bond length for M = Pb increases sharply (2.35 Å). When four [OPb_4] tetrahedra are linked *via* a single edge so that a tetrahedron is edge-linked to two others and corner-linked to the fourth, the bond length also increases (2.40 Å). We may note that in the last case we did not take into account in the calculation of the M – O bond length the type *L*12 layered [OPb] complexes in which all the corners of the [OPb_4] tetrahedron are shared in this way. For these complexes, the M – O bond length is on average 2.34 Å (24 bonds were taken into account) (the limits of their variation were 2.31 – 2.36 Å), *i.e.* smaller by 0.06 Å than for the analogous corners in the remaining complexes. Overall, one may say that an increase in the number of [OM_4] tetrahedra converging at one M corner induces an increase in the M – O bond length.

‡ Only data for [OM_4] complexes with a single cation M were used for the analysis.

Table 13. The M – O bond lengths for M corners with different connectedness in [OM_4] tetrahedra.

Corner of tetrahedron [a]	Number of tetrahedra converging at one M corner	Number of compounds taken into account	Number of bonds taken into account	$(M-O)_{av}$ /Å	Limits of variation of M – O /Å
Cu – O					
	1	15	43	1.92	1.90 – 1.95
	2	13	38	1.92	1.86 – 2.00
	2	10	36	1.94	1.81 – 2.00
	4	2	8	1.96	1.91 – 2.02
Pb – O					
	1	5	11	2.26	2.18 – 2.32
	2	5	7	2.25	2.20 – 2.34
	2	11	38	2.27	2.23 – 2.32
	3	5	15	2.27	2.19 – 2.34
	3	3	19	2.35	2.34 – 2.37
	4	8	33	2.40	2.39 – 2.41

[a] The filled circle designates the corner where two tetrahedra are linked and the numeral 2 at the filled circle indicates that a further two tetrahedra are attached to the given tetrahedron *via* a corner; the semibold edge signifies that yet another tetrahedron has been attached to the given tetrahedron *via* an edge.

VIII. Conclusion

The topological types of the structural units based on oxocentred [OM_4] tetrahedra have been described in the present review. In all, 63 different [OM_4] polyions have been identified; 6 finite, 16 chain, 20 layered, and 21 framework polyions. Since the aim of the present review was the discovery and systematic topological treatment of the oxocentred complexes, we have hardly touched upon the analysis of the geometrical and energetic characteristics of specific crystal structures and on their relation with the type of organisation of the [OM_4] tetrahedra to form a complex. Only the relation between the physical properties of the compounds containing [OM_4] groups and the characteristic features of the linking of these tetrahedra into a complex has been illustrated (for georgbokiite). The studies initiated will be continued by a detailed analysis of the lengths and angles in various types of oxocentred complexes, the study of the correlation of the structures of the compounds described from the standpoint of the crystal chemistry of oxocentred complexes with the properties of these compounds, the discovery of a relation between the traditional and proposed methods for the description of structures, and questions concerning the existence of oxocentred complexes in noncrystalline media, for example in gases.

In writing the review, the authors widely employed the structural data bank Inorganic Crystal Structure Database (ICSD) supplied free of charge to the Department of Crystallography of the St.Petersburg University by Prof. H Bradaczek of the Free University of Berlin. The authors are grateful to Prof. P M Zorkii for valuable advice in connection with the discussion of the review. The review has been written with the financial support of the Russian Foundation for Basic Research (Project No. 96-05-65576) and also of the 'Central Europe' section of the Russian Academy of Natural Sciences.

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