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A comparative crystallochemical analysis of binary compounds and simple anhydrous salts containing pyramidal anions *L*O$_3$ (*L* = S, Se, Te, Cl, Br, I)

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A comparative analysis of binary compounds and 61 simple anhydrous salts $M_y(LO_3)_z$ (L = S, Se, Te, Cl, Br, I) was performed using the crystallochemical program package *TOPOS*. A topological similarity was found between the salts and six types of binary compounds (NaCl, NiAs, $PoCl_2$, Tl_2S_2, ZnTe, rutile). It is notable that these structure relationships are typical for other groups of inorganic salts: borates, carbonates, nitrates, orthophosphates, orthoarsenates, sulfates, selenates, perchlorates, molybdates and halogenides of *d*-metals. For all the $M_y(LO_3)_z$ compounds the topology and uniformity of the ion arrays were investigated. It has been established that in 36 out of the 61 salts at least one ion array has the topology of close packing or the body-centred cubic lattice. The results obtained have allowed us to come to conclusions about the structure-forming role of the arrays of various chemical composition.

1. Introduction

The crystallochemical description of ionic compounds is usually based on the model of close packing of large anions with the voids being occupied by smaller cations. The arrangement of cations is assumed to be predetermined by the type of an anion packing, which is considered as a main structure-forming constituent, whereas the cations distort the anion packing. However, in the last 20 years crystal chemists have been increasingly focusing on the model of cation arrays (O'Keeffe & Hyde, 1985; Vegas, 2000; Vegas & Jansen, 2002). This model ascribes the leading role to cation arrays (sublattices, or subnets) that form a stable three-dimensional periodic structure owing to long-range forces. Vegas & Jansen (2002) systematically investigated about 100 $M_y(TO_4)_z$ salts, and revealed close relationships in the architecture of the cation arrays and some binary compounds. Namely, the spatial arrangement of the cation constituent follows the motif of a binary compound, and the oxygen anions affect the cation sublattice like an applied pressure.

In recent papers (Blatov & Zakutkin, 2002; Ilyushin *et al.*, 2004; Peskov & Blatov, 2004) a number of examples substantiating the model of cation arrays have been found by means of automatized computer crystallochemical analysis. The results obtained showed structural similarities between many types of A_yX_z binary compounds and inorganic anhydrous salts containing triangular (borates, carbonates, nitrates) or tetrahedral (orthosilicates, orthogermanates, orthophosphates *etc.*) anions. It was found that O atoms gave up the structure-forming role in favour of positive-charged central atoms of oxo-anions, whose spatial arrangement followed the motif of one of the ion constituents of a binary compound. This study develops our investigations of structure relationships in the families of binary and ternary substances. Below we consider the crystal structures of the binary compounds A_yX_z and the salts $M_y(LO_3)_z$ with pyramidal anions LO_3 (L = S, Se, Te, Cl, Br, I).

2. Experimental

Crystal structure information on 12 simple sulfites, 24 selenites, three tellurites, 11 chlorates, seven bromates and four iodates of composition $M_y(LO_3)_z$ (L = S, Se, Te, Cl, Br, I; y = 1–2, z = 1–3) was obtained from the ICSD (release 2005/1). The crystal structures determined with low precision ($R_f >$ 10%) or containing disordered O atoms were omitted. Chemical bonds in the crystal structures were determined using the program *AutoCN*; the topological analysis and classification of the substances were performed by means of the program *IsoTest*. The depth of the topological analysis was usually restricted to five coordination spheres of atoms. In most cases such a depth is sufficient to distinguish the topologies of atomic nets. However, coordination sequences $\{N_k\}$[1] up to k = 12 and extended Schläfli symbols (O'Keeffe *et al.*, 2000) were calculated using the program *ADS* (Blatov *et al.*, 2000) for some cases that required a more detailed topological description. All three computer programs are parts of the crystallochemical software package *TOPOS* (Blatov *et al.*, 2000). Two compounds were related to the same topological type, and called isotypic, if they had equal sets of $\{N_k\}$ for all corresponding atoms. Similarly, two compounds were related to the same structure type, and called isostructural, if the space groups, Wyckoff positions and coordination numbers (CN, N_1) of corresponding atoms were coincident (Lima-de-Faria *et al.*, 1990). Besides searching for strict structural relationships, when the coordination sequences $\{N_k\}$ of corresponding atoms are the same, the crystal structures are of interest, whose $\{N_k\}$ are different but whose N_k values are close to one another at any k (Blatov, 2001). In this case of nonstrict isotypism there is no full topological equality, but the crystal structures are closely related.

The topology of the substances $M_y(LO_3)_z$ was investigated in two representations: complete and quasi-binary. In the former representation all the atoms M, L and O are considered, while in the latter the anions $[LO_3]$ are described as structureless quasi-particles $[L]$, but their connections with the metal atoms M are retained. Thus, the quasi-binary representation ignores the coordination type of the complex groups $[LO_3]$, or the method of the M–$[LO_3]$ connection, and the ternary compound is represented as a binary $M_y[L]_z$. Full topological similarity of binary and ternary compounds can exist only as a kind of approximate isotypism (Blatov & Zakutkin, 2002), when at least two sorts of chemically equivalent atoms are topologically non-equivalent in the binary compound, or two chemically different atoms of the ternary compound belong to the same topological sort. If a ternary compound is considered in a quasi-binary representation $M_y[L]_z$, one can find its partial isotypism with a binary compound A_yX_z, when the $[L]$ particle corresponds to an A or X atom.

As before (Peskov & Blatov, 2004), the crystal structures of the salts were compared with binary compounds. For this purpose we have used the database (Blatov & Zakutkin, 2002) presently containing information on 1835 archetypes of topological types of the A_yX_z compounds, and the database on the topology of 1965 ideal nets including all the topological types from the RCSR (Reticular Chemistry Structure Resource, http://reticularchemistry.net/RCSR/).

Lastly we have analyzed the topology and uniformity of all ion arrays in the $M_y(LO_3)_z$ salts; the results have allowed us to come to conclusions about the structure-forming role of the arrays of various composition. The close-packing topology was detected using the program *IsoTest* by comparing coordination sequences $\{N_k\}$ of all ions of the array with a set of $\{N_k\}$ typical for close packing. To assess the uniformity of an ion array we have used the root-mean-square error of the lattice quantizer (G_3) (Blatov, 2001),

$$G_3 = \frac{1}{3}\frac{1}{Z}\sum_{i=1}^{Z}\int_{\mathrm{VDP}(i)} R^2\,\mathrm{d}V_{\mathrm{VDP}(i)} \Bigg/ \left\{\frac{1}{Z}\sum_{i=1}^{Z} V_{\mathrm{VDP}(i)}\right\}^{5/3}, \quad (1)$$

where Z is the number of atoms in the asymmetric unit, the volume integration is performed over the Voronoi–Dirichlet polyhedra (VDP) of the atoms, and R is the distance between the atom and a point inside its VDP. It is known (Blatov, 2001) that the smaller the G_3 value the more uniform the spatial arrangement of the ions. The body-centred cubic (b.c.c.) lattice has the smallest G_3 (0.07854), whereas close packings are less uniform (G_3 = 0.07875). Using the G_3 criterion one can choose the most significant array in a three-dimensional net. Peresypkina & Blatov (2003) have shown that the most uniform array is structure-forming, *i.e.* it causes a three-dimensional symmetry of the crystal structure.

3. Topological analysis of the crystal structures of simple sulfites, selenites, tellurites, chlorates, bromates and iodates

3.1. Complete representation

The crystallochemical analysis of the $M_y(LO_3)_z$ salts allows us to arrange them into 32 topological and 32 structural types (Tables 1 and 2). As a rule, the topological and structural types are the same, but there can be two non-trivial relationships between them:

(i) Isotypic compounds can be classified with several structure types. This case can exist if two atomic nets have the same topology but different space groups, and/or their atoms are assigned to different Wyckoff positions. It occurs rather frequently (Blatov & Zakutkin, 2002; Peskov & Blatov, 2004), thus the topological type K_2SO_3 includes three structural types, K_2SO_3, Na_2SO_3 and Cs_2TeO_3, with similar structures, but different space-group symmetry (Table 1).

(ii) Isostructural compounds have similar geometrical parameters but different topologies, and hence are related to

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[1] N_k is the number of atoms in the kth coordination sphere of a given atom.

Table 1

Arrangement of simple sulphites, selenites and tellurites $M_y(LO_3)_z$ (L = S, Se, Te) into topological and structure types.

Quasi-binary representation $M_y[L]_z$	Full representation			
Topological type		Structure type	Space group	Collection code†
$Fe[SO_3]$	$FeSO_3$	$CdSO_3$-III	$R\bar{3}$	62642
		$FeSO_3$		14190
		α-$MnSO_3$		15554
$K_2[SO_3]$	K_2SO_3	K_2SO_3	$P\bar{3}m$	60762
		Cs_2TeO_3	$P32$	59164
		Na_2SO_3	$P\bar{3}$	4432
	Na_2SO_3	K_2TeO_3	$P\bar{3}$	65640
		Na_2SO_3		31816
β-$Zn[SeO_3]$	β-$ZnSeO_3$	$CuSeO_3$-II	$Pcab$	29506
		β-$ZnSeO_3$	$Pbca$	29500
$Mn[SeO_3]$	$MnSeO_3$	$CdSeO_3$	$Pnma$	75273
		$CoSeO_3$		496
		$CuSeO_3$		498
		α-$HgSeO_3$		79694
		$MnSeO_3$		495
		$NiSeO_3$		497
$La_2[SeO_3]_3$	$La_2(SeO_3)_3$	$La_2(SeO_3)_3$	$Pnma$	410952
$Pb[SO_3]$	$PbSO_3$	$PbSO_3$	$Pnma$	68889
	$PbSO_3$ (scotlandite)	$BaSeO_3$	$P2_1/m$	54156
		$PbSO_3$ (scotlandite)		30993
		$PbSeO_3$ (molybdomenite)		1271
β-$Mn[SO_3]$	β-$MnSO_3$	β-$MnSO_3$	$P2_1/a$	26556
	$CdSO_3$-II	$CdSO_3$-II	$P2_1/c$	62641
		$CdSeO_3$		75274
$Ag_2[SO_3]$	Ag_2SO_3	Ag_2SO_3	$P2_1/c$	4433
$Cd[SO_3]$-I	$CdSO_3$-I (γ-$HgSeO_3$)	$CdSO_3$-I	$P2_1/c$	62640
		γ-$HgSeO_3$		412548
β-$Hg[SeO_3]$	β-$HgSeO_3$	β-$HgSeO_3$		412547
$Ag_2[SeO_3]$	Ag_2SeO_3	Ag_2SeO_3	$P2_1/c$	78388
		Na_2SeO_3		280941
α-$Pb[SeO_3]$	α-$PbSeO_3$	α-$PbSeO_3$	$P2_1/c$	94763
$Co[SeO_3]$-II	$CoSeO_3$-II	$CoSeO_3$-II	$C2/c$	80401
$Bi_2[SeO_3]_3$	$Bi_2(SeO_3)_3$	$Bi_2(SeO_3)_3$	$P2_1/n$	409478
$Ce[SeO_3]_2$	$Ce(SeO_3)_2$	$Ce(SeO_3)_2$	$P2_1/n$	60778
$Cu[SeO_3]$-III	$CuSeO_3$-III	$CuSeO_3$-III	$P2_1/n$	29507
$Ti[SeO_3]_2$	$Ti(SeO_3)_2$	$Mn(SeO_3)_2$	$P2_1/n$	69801
		$Ti(SeO_3)_2$	$P2_1/c$	200203
$Rb_2[TeO_3]$	Rb_2TeO_3	Rb_2TeO_3	$C2/m$	38223
$Cu[SeO_3]$-IV	$CuSeO_3$-IV	$CuSeO_3$-IV	$P\bar{1}$	29508

† ICSD collection codes are given.

Table 2

Arrangement of simple chlorates, bromates and iodates $M(LO_3)_z$ (L = Cl, Br, I) into topological and structure types.

Quasi-binary representation $M[L]_z$	Full representation			
Topological type		Structure type	Space group	Collection code†
$Na[ClO_3]$-I	$NaClO_3$-I	$NaClO_3$-I	$P2_13$	80340
		$NaBrO_3$		47174
	NH_4ClO_3	$CsBrO_3$	$R3m$	74769
		$KClO_3$-HP, LT-II		9483
		$KBrO_3$		47173
		NH_4ClO_3		23935
		$RbClO_3$		10283
		$RbBrO_3$		74768
		$TlClO_3$		76434
		$TlBrO_3$		76966
	$KClO_3$-HT	$KClO_3$-HT	$Pcmn$	16690
	$KClO_3$	$KClO_3$	$P2_1/m$	26409
α-$Li[IO_3]$	α-$LiIO_3$	α-$LiIO_3$	$P6_3$	46025
	$NaIO_3$	$NaIO_3$	$Pbnm$	202679
$Ag[ClO_3]$	$AgClO_3$	$AgClO_3$	$I4/m$	30227
$Ba[ClO_3]_2$	$Sr(ClO_3)_2$	$Sr(ClO_3)_2$	$Fdd2$	61157
		$Pb(ClO_3)_2$		40286
	$Ba(ClO_3)_2$	$Ba(ClO_3)_2$	$Fdd2$	40285
		$Ba(BrO_3)_2$-II		40287
$Na[IO_3]$	$NaIO_3$	$NaIO_3$	$Pbn2_1$	20168
γ-$Li[IO_3]$	γ-$LiIO_3$	γ-$LiIO_3$	$Pna2_1$	201817
$Ba[BrO_3]_2$-I	$Ba(BrO_3)_2$-I	$Ba(BrO_3)_2$-I	$C2/c$	66035

† ICSD collection codes are given.

different topological types. This variant can occur if the $\{N_k\}$ values of the compounds are different at $k \geq 2$, but it has never been spotted. Probably the first such examples are the pairs β- and γ-$HgSeO_3$ (Weil, 2002), $PbSO_3$ (*Pnma*) (Christensen & Hewat, 1990) and high-temperature $KClO_3$. Thus, despite similar unit-cell dimensions and the same space-group symmetry, the coordination sequences of β- and γ-$HgSeO_3$ differ even in the second coordination sphere (Table 3). Note that these phases have the same numbers of symmetrically inequivalent atoms but unequal numbers of topologically non-equivalent ones: in γ-$HgSeO_3$ two inequivalent atoms are joined in the same topological sort. The topological differences are caused by different coordination types of selenite ions (Table 3): in the β-phase each SeO_3^{2-} anion is bonded with N_2 = 6 Hg atoms (one of them is chelate-coordinated), but in γ-$HgSeO_3$ the Se atoms have N_2 = 5, and SeO_3^{2-} anions have the coordination type T^{32} (two Hg atoms are chelate-coordinated)[2]. In the second example the crystal structures of $PbSO_3$ and $KClO_3$ have equal numbers of topologically non-equivalent atoms and the oxo-anions are of the same coordination type despite significantly different unit-cell dimensions (Table 3). Here the discrepancies in $\{N_k\}$ arise at k = 3; they are caused by different numbers of the 6- and 8-circuits (closed chains of connected atoms) meeting in Pb^{2+} and K^+ cations (see the Schläfli symbols in Table 3).

A comparative analysis of six families of ternary compounds reveals 11 cases of topological relationships. Sulfites and selenites are isotypic in three cases: $PbSO_3$ (scotlandite) and $PbSeO_3$ (molybdomenite); $CdSO_3$-I and γ-$HgSeO_3$; $CdSO_3$-II and $CdSeO_3$. Cs_2TeO_3 and K_2TeO_3 have topological analogs among sulfites (K_2SO_3 and Na_2SO_3 [CC = 31816][3], respectively). Many more structural correlations were found between simple chlorates and bromates. In particular, isotypism was revealed for the pairs $NaClO_3$-I (Sowa, 1995) and $NaBrO_3$; $Ba(ClO_3)_2$ and $Ba(BrO_3)_2$-II (Lutz *et al.*, 1989); and in the group of rhombohedral NH_4ClO_3, $KClO_3$-HP, $RbClO_3$, $TlClO_3$, $KBrO_3$, $RbBrO_3$, $CsBrO_3$ and $TlBrO_3$. Topological and geometrical similarities of chlorates, sulfites

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[2] Hereafter the coordination types are given in the notation of Serezhkin (1986). The letter X in the symbol X_{mbtk} shows the ligand denticity (M, B, T or K for mono-, bi-, tri- or tetradentate ligands, respectively), the numbers *mbtk*… designate the numbers of the complexing atoms connected to one, two, three or four atoms of the ligand.

[3] Hereafter, collection codes (CC) in the ICSD (release 2005/1) are given in brackets.

Table 3
Coordination sequences and short Schläfli symbols for two modifications of $HgSeO_3$, $PbSO_3$ (*Pnma*) and $KClO_3$.

Compound	Space group	Unit-cell dimensions a (Å)	b (Å)	c (Å)	β (°)	LO_3 coordination type†	Atom	N_1	N_2	N_3	N_4	N_5	Schläfli symbol‡
β-$HgSeO_3$	$P2_1/c$	4.361	10.220	7.119	102.7	T^{51}	Hg	7	13	38	45	111	$4^4\ 6^9\ 8^7\ 10$
							Se	3	6	28	39	93	$4\ 6^2$
							O(1)	3	12	19	56	63	$4^2\ 6$
							O(2)	3	13	23	64	71	4 6 8
							O(3)	4	18	24	65	70	$4^2\ 6^4$
γ-$HgSeO_3$		4.738	9.053	7.146	92.06	T^{32}	Hg	7	11	32	36	87	$4^6\ 6^6\ 8^7\ 10^2$
							Se	3	5	24	32	78	$4^2\ 6$
							O(1,2)	3	12	18	51	55	$4^2\ 6$
							O(3)	4	16	20	54	55	$4^4\ 6^2$
$PbSO_3$	*Pnma*	7.925	5.485	6.816		T^{33}	Pb	9	16	57	64	158	$4^{11}\ 6^{13}\ 8^{12}$
							S	3	6	36	46	131	4^3
							O(1)	4	22	31	96	97	$4^4\ 6^2$
							O(2)	4	21	31	95	96	$4^5\ 6$
$KClO_3$-HT	*Pcmn*	4.740	5.640	13.800		T^{33}	K	9	16	56	62	152	$4^{11}\ 6^{15}\ 8^{10}$
							Cl	3	6	36	46	128	4^3
							O(1)	4	22	32	94	96	$4^4\ 6^2$
							O(2)	4	21	30	92	92	$4^5\ 6$

† According to Serezhkin (1986). ‡ Only total numbers of rings of a given size are specified for short.

and selenites were discovered in three cases. Thus, $KClO_3$ (Danielsen *et al.*, 1981) and scotlandite; $NaIO_3$ (space group *Pbnm*; Svensson & Stahl, 1988) and $MnSeO_3$ are both isostructural and isotypic, whereas the high-temperature phase of $KClO_3$ merely corresponds geometrically to the orthorhombic $PbSO_3$.

In all of these cases topological relationships between the salts $M_y(LO_3)_z$ (L = S, Se, Te, Cl, Br, I) also mean a geometrical similarity, *i.e.* variations in chemical composition do not lead to essential structure distortions (Tables 1 and 2).

Table 4
Topological similarities between the $M_y(LO_3)_z$ (L = S, Se, Cl, Br, I) and A_yX_z compounds.

Topological type	A_yX_z	Sublattice†	N_1	N_2	N_3	N_4	N_5
$KClO_3$	NaCl	M; Na; [LO_3]; Cl	6	18	38	66	102
$KClO_3$-HT							
$NaClO_3$-I							
NH_4ClO_3							
$PbSO_3$ (scotlandite)							
$PbSO_3$ (*Pnma*)							
α-$LiIO_3$	NiAs	M; Ni	6	20	42	74	114
$MnSeO_3$		[LO_3]; As	6	18	42	74	114
$NaIO_3$ (*Pbnm*)							
$Ba(BrO_3)_2$-I	$PoCl_2$	Ba; Po	8	14	56	50	152
	[CC = 26650]	[BrO_3]; Cl(1, 2)	4	20	28	94	76
$AgClO_3$	Tl_2S_2-I	Ag(1); Tl(1)	8	26	56	98	152
	[CC = 78161]	Ag(2); Tl(2)	4	14	44	90	144
		[ClO_3]; S	6	21	50	93	148
β-$ZnSeO_3$	ZnTe	Zn; [SeO_3]; Te	5	14	29	50	77
$Ti(SeO_3)_2$	TiO_2	Ti; Ti	6	10	38	34	102
	(rutile)	[SeO_3]; O	3	14	19	62	51

† Topologically equivalent (with the same coordination sequences {N_1, N_2, N_3, N_4, N_5}) ion sublattices are given.

3.2. Quasi-binary representation

Simplification of the topology of ternary compounds in a quasi-binary representation results in additional topological relationships (Tables 1 and 2). Thus, in the family of quasi-binary sulfites, selenites and tellurites there are three such cases: between K_2SO_3, two phases of Na_2SO_3, K_2TeO_3 and Cs_2TeO_3; between lead sulfites, lead selenite and $BaSeO_3$; between $CdSO_3$-II, $CdSeO_3$ and β-$MnSO_3$. In fact, the similarity of topological types in the quasi-binary representation means a topological equivalence of mixed packings of cations and structureless anions. In particular, different coordination types of anions are ignored in K_2SO_3 (T^{631}) and Na_2SO_3 (T^{901}) [CC = 31816]; only the total number of coordinated cations (6 + 3 + 1 = 9 + 0 + 1) is important. The new relationships in the group of halogenates are also notable: four structural types ($NaClO_3$-I, NH_4ClO_3 and two phases of $KClO_3$) become similar in a quasi-binary representation. Besides, the same topological types are formed by the chlorates $M(ClO_3)_2$ (space group *Fdd2*) and by α-$LiIO_3$ (Svensson *et al.*, 1983) and $NaIO_3$ (space group *Pbnm*).

3.3. Relations to binary compounds

There are no cases of full topological similarity between the $M_y(LO_3)_z$ and A_yX_z substances; however, we have found six examples of partial isotypism (Table 4). The most numerous is the group of $M_y(LO_3)_z$ crystal structures with NaCl (**pcu-b**)[4] topology. For instance, the correspondence of the NaCl and $NaClO_3$ crystal structures has been well known if one considers the $[ClO_3]^-$ anion as a whole (Fig. 1*a*), but the

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[4] Hereafter the RCSR names (if any) are given for the topological types of binary compounds.

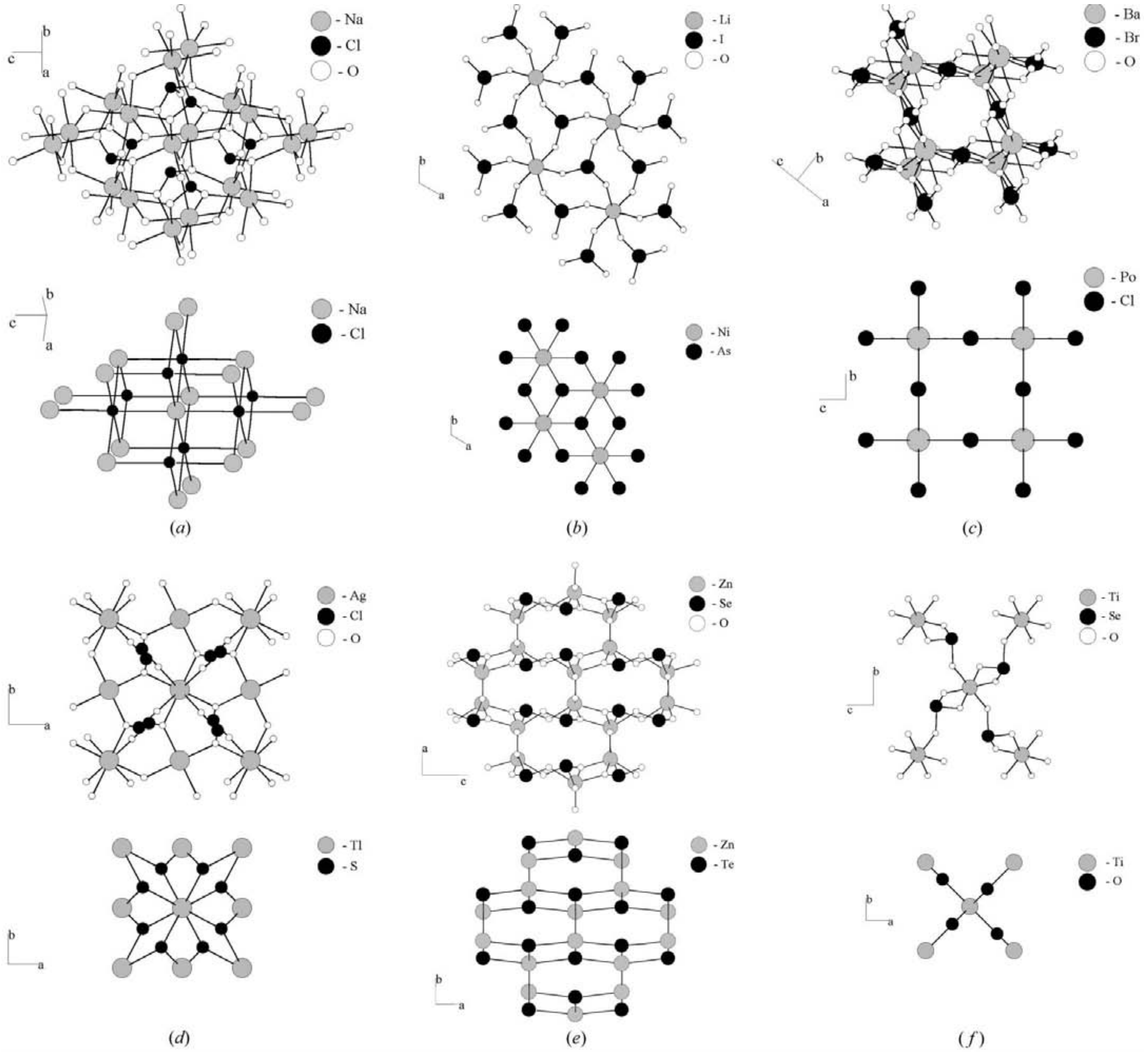

Figure 1
Topological similarities between the crystal structures of chalcogenites, halogenates and binary compounds: (*a*) $NaClO_3$-I and NaCl; (*b*) α-$LiIO_3$ and NiAs; (*c*) $BaBrO_3$-I and $PoCl_2$; (*d*) $AgClO_3$ and Tl_2S_2-I; (*e*) β-$ZnSeO_3$ and ZnTe; (*f*) $Ti(SeO_3)_2$ and TiO_2 (rutile).

topological similarity between NaCl, scotlandite (Pertlik & Zemann, 1985) and orthorhombic $PbSO_3$ (Christensen & Hewat, 1990) has newly been discovered. Besides, the NaCl topological analogs were first found among selenites (molybdomenite and $BaSeO_3$) and some chlorates (NH_4ClO_3 and two phases of $KClO_3$). The second by frequency NiAs topological motif (**nia**) is realised in $MnSeO_3$, α-$LiIO_3$ (Svensson *et al.*, 1983) (Fig. 1*b*) and $NaIO_3$ (space group *Pbnm*; Svensson & Stahl, 1988). Note that the NaCl and NiAs topological motifs have been recently found in borates, carbonates, nitrates (Blatov & Zakutkin, 2002), orthophosphates, orthoarsenates, sulfates, selenates, perchlorates, molybdates (Vegas & Jansen, 2002; Ilyushin *et al.*, 2004) and complex halogenides of *d*-metals (Peskov & Blatov, 2004).

The $PoCl_2$ motif (**scu**), being rare among inorganic salts, is realised in $Ba(BrO_3)_2$-I (Lutz *et al.*, 1990) (Fig. 1*c*); it was previously found only in the complex halogenides of *d*-metals (Peskov & Blatov, 2004). At the same time the crystal structure of $AgClO_3$ is the first example of a ternary compound with the $Tl^{I}Tl^{III}S_2$ topology (Fig. 1*d*). Also the topological similarity of ZnTe (**bnn**) and β-$ZnSeO_3$ (Bensch & Günter, 1986) has never been known (Fig. 1*e*). Note that, in all of the cases of relationships between binary and ternary compounds, similarly charged ion sublattices correspond to each other.

Table 5
Coordination sequences and extended Schläfli symbols for closely related sulphites and iodates $M_y[L]_z$ (quasi-binary representation) and binary compounds.

Compound	Sublattice	N_1	N_2	N_3	N_4	N_5	N_6	N_7	N_8	N_9	N_{10}	N_{11}	N_{12}	Schläfli symbols
Cd[SO$_3$]-I	Cd	5	15	33	58	89	127	173	226	285	351	425	506	$4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 6_2\ 6_2\ 6_4\ 6_4\ 6_5$
(L = SO$_3$)	L	5	15	33	58	89	127	173	226	285	351	425	506	$4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 6_2\ 6_3\ 6_4\ 6_4\ 6_4$
SnP	Sn, P	5	16	33	58	89	128	173	226	285	352	425	506	$4_1\ 4_1\ 4_1\ 4_1\ 6_3\ 6_3\ 6_5\ 6_5\ 6_5\ 6_5$
Na[IO$_3$]	Na	6	16	42	72	114	162	222	288	366	450	546	648	$4_1\ 4_1\ 4_1\ 4_1\ 4_3\ 4_3\ 4_3\ 4_3\ 6_2\ 6_2\ 6_5\ 6_5\ 6_5\ 6_5\ 8_{82}$
(L = IO$_3$)	L	6	20	42	74	114	164	222	290	366	452	546	650	$4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_2\ 4_2\ 4_2\ 6_6\ 6_6$
NiAs	Ni	6	20	42	74	114	164	222	290	366	452	546	650	$4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 6_4\ 6_4\ 6_4$
	As	6	18	42	74	114	162	222	290	366	450	546	650	$4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_1\ 4_2\ 4_2\ 4_2\ 6_8\ 6_8\ 6_8\ 6_8\ 6_8\ 6_8$

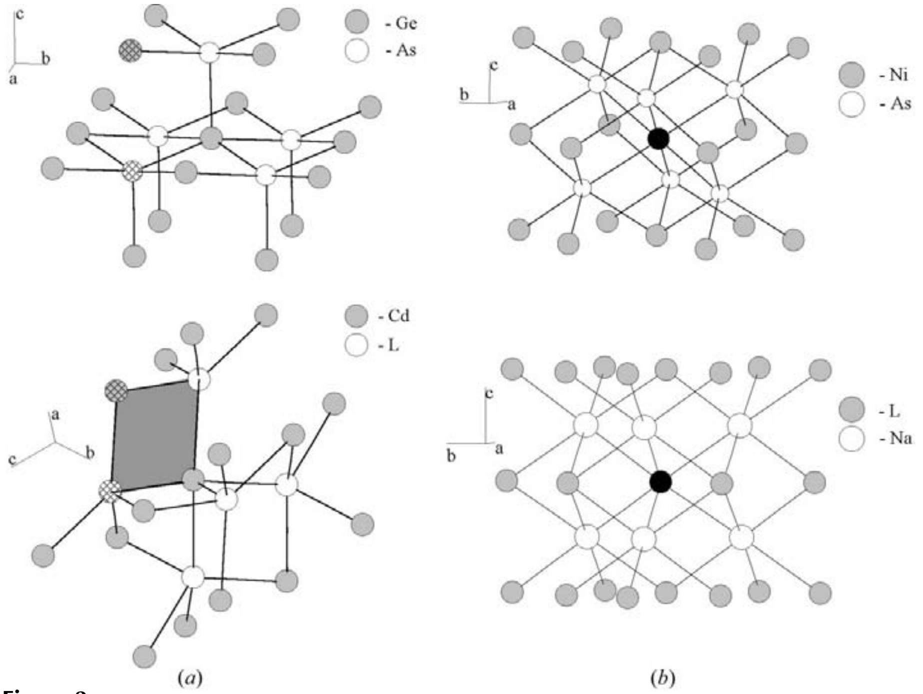

Figure 2
Examples of nonstrict partial isotypism between binary and ternary compounds. (*a*) GeAs (SnP structural type) and Cd[L] (L = SO$_3$). An additional 4-circuit is shaded which appears thanks to a contact between Cd^{2+} and SO$_3^{2-}$ ions. The Cd^{2+} and SO$_3^{2-}$ ions are hatched together with corresponding atoms in the SnP crystal structure. (*b*) NiAs and Na[L] (L = IO$_3$). Two coordination spheres are shown for black (Ni or L) nodes.

An important feature of simple selenites is their relation to another well known topological type, TiO$_2$ (rutile, **rtl**). Ti(SeO$_3$)$_2$ (Fig. 1*f*) and Mn(SeO$_3$)$_2$ have the **rtl** topology, whereas other previously studied inorganic salts with triangular or tetrahedral anions never follow this motif.

Two cases of nonstrict partial isotypism were found between the $M_y(LO_3)_z$ and A_yX_z compounds. Thus, according to Table 5, the N_k values for ion sublattices in SnP (**sqp**) [CC = 16077] and CdSO$_3$-I (quasi-binary representation) differ only by unity at k = 2, 6, 10, ... This difference is independent of k, and for k = 2 is caused by a contact between the Cd^{2+} ion and the sulfite group (Fig. 2*a*), while there is no such contact between corresponding Sn and P atoms. As a result, there appear additional 4-circuits in CdSO$_3$-I (Table 5), one of which is selected in Fig. 2(*a*). Note that CdSO$_3$-I is a very rare case of nets where the different topological sorts of nodes (Cd and L) cannot be distinguished by coordination sequences only; the Schläfli symbols should be considered in addition (Table 5).

By comparing atomic coordination sequences one can find a topological similarity that is very difficult to discover visually. An illustration is the pair NiAs (**nia**) and NaIO$_3$ (Table 5). The coordination sequences of these nets are very close; the difference in the N_k values reaches two, but remains constant when k increases. Fig. 2(*b*) shows that this difference is caused by different coordination types of structural units; however, the similarity is rather clear within the first two coordination spheres. A visual analysis of high-order coordination spheres is practically impossible owing to the topological complexity of the nets.

3.4. Topology of ion arrays

The topological analysis of ion arrays shows that in more than half of $M_y(LO_3)_z$ crystal structures (36 out of 61) at least one array can be found with the topology of close packing or the b.c.c. lattice (Tables 6 and 7). In most cases such special topologies occur in the ion arrays {M,L} (25 compounds) and/or {L} (12 compounds). In the crystal structures of eight chlorates and bromates the sublattices {M,L} and {M,O} follow the b.c.c. and hexagonal close-packed (h.c.p.) motifs, respectively. Besides, in two selenites and three halogenates the M atoms are arranged as in the b.c.c. or face-centred cubic (f.c.c.) lattices. At the same time O atoms prefer non-close-packing motifs: only in potassium tellurite the {O} array has the h.c.p. topology.

Analysis of the uniformity of the ion arrays also justifies an important role of the mixed arrays {M,L}: they have the smallest G_3 values in 45 out of 61 compounds. The role of the {L} sublattices is far less significant: they are the most uniform only in four salts (Ag$_2$SO$_3$, CdSO$_3$-I, CoSeO$_3$-II and γ-LiIO$_3$). The role of the mixed arrays can be explained by considering the sizes of the M and L particles. Matching the particle sizes has to increase the array uniformity; therefore the most uniform arrays are usually formed by large M cations together with the closest by size LO_3 anions. Besides, the charges of

Table 6

G_3 values for the most uniform ion arrays in the crystal structures of the $M_y(LO_3)_z$ compounds (L = S, Se, Te).

Topology of ion array	Compound	Most uniform array†	G_3	Collection code‡
Sulphites				
b.c.c. (M,L)	K_2SO_3	$\{M,L\}$	0.0786	60762
h.c.p. (L)		$\{L\}$	0.0833	
b.c.c. (M,L)	Na_2SO_3 [CC = 4432]	$\{M,L\}$	0.0787	4432
	Na_2SO_3 [CC = 31816]			31816
b.c.c. (L)	Ag_2SO_3	$\{L\}$	0.0795	4433
h.c.p. (L)	$CdSO_3$-I	$\{L\}$	0.0799	62640
	$PbSO_3$ (*Pnma*)	$\{M,L\}$	0.0809	68889
		$\{M\}$	0.0816	
	$PbSO_3$ (scotlandite)	$\{M,L\}$	0.0811	30993
		$\{M\}$	0.0814	
	$CdSO_3$-II	$\{M,L\}$	0.0817	62641
	$CdSO_3$-III		0.0818	62642
	$FeSO_3$		0.0818	14190
	α-$MnSO_3$		0.0819	15554
	β-$MnSO_3$		0.0818	26556
Selenites				
b.c.c. (M,L)	$CuSeO_3$ (*Pnma*)	$\{M,L\}$	0.0791	498
h.c.p. (L)		$\{L\}$	0.0829	
f.c.c. (M,L)	Ag_2SeO_3	$\{M,L\}$	0.0790	78388
h.c.p. (L)		$\{L\}$	0.0832	
	Na_2SeO_3	$\{M,L\}$	0.0792	280941
		$\{L\}$	0.0820	
b.c.c. (M,L)	$CdSeO_3$ (*Pnma*)	$\{M,L\}$	0.0792	75273
	$CoSeO_3$ (*Pnma*)		0.0791	496
	α-$HgSeO_3$		0.0790	79694
	$MnSeO_3$		0.0792	495
	$NiSeO_3$		0.0792	497
b.c.c. (M)	$Ti(SeO_3)_2$	$\{M\}$	0.0809	200203
f.c.c. (L)	$CuSeO_3$-II	$\{M,L\}$	0.0813	29506
		$\{L\}$	0.0827	
	β-$ZnSeO_3$	$\{M,L\}$	0.0815	29500
		$\{L\}$	0.0825	
h.c.p. (L)	γ-$HgSeO_3$	$\{L\}$	0.0820	412548
		$\{M,L\}$	0.0830	
f.c.c. (M,L)	$CuSeO_3$-IV	$\{M,L\}$	0.0821	29508
		$\{L\}$	0.0827	
f.c.c. (M)	$Mn(SeO_3)_2$	$\{M\}$	0.0797	69801
		$\{L\}$	0.0798	
	$CuSeO_3$-III	$\{M,L\}$	0.0832	29507
		$\{L\}$	0.0839	
	$BaSeO_3$	$\{M,L\}$	0.0809	54156
		$\{M\}$	0.0818	
	$Bi_2(SeO_3)_3$	$\{M,L\}$	0.0820	409478
	$La_2(SeO_3)_3$		0.0813	410952
	$CdSeO_3$ ($P2_1/c$)	$\{M,L\}$	0.0814	75274
	β-$HgSeO_3$		0.0807	412547
	$PbSeO_3$ (molybdomenite)		0.0807	1271
	α-$PbSeO_3$		0.0804	94763
	$Ce(SeO_3)_2$	$\{M,L\}$	0.0802	60778
	$CoSeO_3$-II	$\{L\}$	0.0834	80401
Tellurites				
b.c.c. (M,L)	K_2TeO_3	$\{M,L\}$	0.0789	65640
h.c.p. (O)		{O}	0.0844	
b.c.c. (M,L)	Rb_2TeO_3	$\{M,L\}$	0.0789	38223
	Cs_2TeO_3		0.0787	59164

† The ion arrays are given that have a special topology or the smallest G_3 value (within the estimated error 0.001). ‡ ICSD collection codes are given.

Table 7

G_3 values for the most uniform ion arrays in the crystal structures of the $M(LO_3)_z$ compounds (L = Cl, Br, I).

Topology of ion array	Compound	Most uniform array†	G_3	Collection code
Chlorates				
b.c.c. (M,L)	$KClO_3$-HP, LT-II	$\{M,L\}$	0.0788	9483
f.c.c. (M,O)		$\{M,O\}$	0.0829	
	NH_4ClO_3	$\{M,L\}$	0.0791	23935
		$\{M,O\}$	0.0814	
	$RbClO_3$	$\{M,L\}$	0.0790	10283
		$\{M,O\}$	0.0820	
	$TlClO_3$	$\{M,L\}$	0.0788	76434
		$\{M,O\}$	0.0828	
f.c.c. (M)	$NaClO_3$-I	$\{M,L\}$	0.0799	80340
f.c.c. (L)		$\{M\}$	0.0823	
		$\{L\}$	0.0836	
	$AgClO_3$	$\{M,L\}$	0.0789	30227
	$Ba(ClO_3)_2$		0.0799	40285
	$KClO_3$		0.0807	26409
	$Pb(ClO_3)_2$		0.0799	40286
	$Sr(ClO_3)_2$		0.0799	61157
	$KClO_3$-HT	$\{M\}$	0.0811	16690
		$\{M,L\}$	0.0814	
Bromates				
b.c.c. (M,L)	$CsBrO_3$	$\{M,L\}$	0.0788	74769
f.c.c. (M,O)		$\{M,O\}$	0.0811	
	$KBrO_3$	$\{M,L\}$	0.0788	47173
		$\{M,O\}$	0.0805	
	$RbBrO_3$	$\{M,L\}$	0.0788	74768
		$\{M,O\}$	0.0805	
	$TlBrO_3$	$\{M,L\}$	0.0787	76966
		$\{M,O\}$	0.0806	
f.c.c. (M)	$NaBrO_3$	$\{M,L\}$	0.0796	47174
f.c.c. (L)		$\{M\}$	0.0830	
		$\{L\}$	0.0843	
	$Ba(BrO_3)_2$-I	$\{M,L\}$	0.0837	66035
	$Ba(BrO_3)_2$-II		0.0797	40287
Iodates				
b.c.c. (M,L)	$NaIO_3$ (*Pbnm*)	$\{M,L\}$	0.0788	202679
	$NaIO_3$ ($Pbn2_1$)		0.0789	20168
f.c.c. (M)	γ-$LiIO_3$	$\{L\}$	0.0824	201817
		$\{M\}$	0.0910	
b.c.c. (L)	α-$LiIO_3$	{O}	0.0826	46025
		$\{L\}$	0.0829	

† The ion arrays are given that have a special topology or the smallest G_3 value (within the estimated error 0.001).

particles can also influence the array uniformity (Peresypkina & Blatov, 2003). Thus, in $Ti(SeO_3)_2$ the high-charged Ti^{4+} cations form a b.c.c. sublattice with the largest uniformity.

It should be noted that in a number of compounds [$PbSO_3$ (space group *Pnma*), $PbSO_3$ (scotlandite), γ-$HgSeO_3$, $CuSeO_3$-II, β-$ZnSeO_3$, $CuSeO_3$-III, $CuSeO_3$-IV, $Mn(SeO_3)_2$, $BaSeO_3$, $KClO_3$-HT and α-$LiIO_3$] ion arrays of different composition compete with one another to be structure-forming. For instance, the arrays $\{L\}$ and $\{M,L\}$ in γ-$HgSeO_3$ are almost equally uniform, because the difference between corresponding G_3 values is equal to the G_3 estimated error (0.001, Table 6). The $\{L\}$ array is probably more likely to be structure forming since it has a special topology (h.c.p.).

To study how the chemical composition of an oxo-anion influences the structure-forming role of ion arrays, we have considered a series of $M_y(LO_3)_z$ salts with different L (Table 8). In each of the series the compounds have the same stoichiometry (y = constant, z = constant) and the same M atom. One can draw the following conclusions using the data from Table 8:

(i) The uniformity of the mixed arrays $\{M,L\}$ (L = S, Se, Te, or L = Cl, Br, I) increases (G_3 values decrease) with increase in

Table 8
Uniformity of ion arrays in series of $M_y(LO_3)_z$ compounds with the same M.

G_3 values for b.c.c. and close-packing arrays are bold-faced and italicized, respectively.

	G_3 values for ion arrays						
Compound	$\{M,L\}$	$\{L\}$	$\{M\}$	$\{M,\mathrm{O}\}$	$\{\mathrm{O}\}$	$\{M,L,\mathrm{O}\}$	$\{L,\mathrm{O}\}$
Chalcogenites							
Ag							
Ag_2SO_3	0.0824	**0.0795**	0.0838	0.0861	0.0893	0.0924	0.0999
Ag_2SeO_3	*0.0790*	*0.0832*	0.0882	0.0862	0.0836	0.0874	0.0934
Cd							
$CdSO_3$-I	0.0834	*0.0799*	0.0837	0.0884	0.0845	0.0936	0.0940
$CdSO_3$-II	0.0817	0.0834	0.0893	0.0957	0.0887	0.0983	0.0964
$CdSO_3$-III	0.0818	0.0839	0.0955	0.0958	0.0891	0.0965	0.0952
$CdSeO_3$ ($P2_1/c$)	0.0814	0.0847	0.0891	0.0958	0.0879	0.0960	0.0934
$CdSeO_3$ (*Pnma*)	**0.0792**	0.0826	0.0828	0.0853	0.0811	0.0874	0.0883
K							
K_2SO_3	**0.0786**	*0.0833*	0.0865	0.0866	0.0903	0.0913	0.1023
K_2TeO_3	**0.0789**	0.0870	0.0880	0.0864	*0.0844*	0.0883	0.0943
Mn							
α-$MnSO_3$	0.0819	0.0837	0.0964	0.0969	0.0891	0.0967	0.0944
β-$MnSO_3$	0.0818	0.0833	0.0889	0.0967	0.0889	0.0981	0.0956
$MnSeO_3$	**0.0792**	0.0827	0.0828	0.0855	0.0807	0.0868	0.0870
Na							
Na_2SO_3 [CC = 4432]	**0.0787**	0.0843	0.0866	0.0861	0.0861	0.0897	0.0969
Na_2SO_3 [CC = 31816]	**0.0787**	0.0848	0.0866	0.0848	0.0869	0.0903	0.0998
Na_2SeO_3	*0.0792*	*0.0820*	0.0873	0.0871	0.0828	0.0879	0.0922
Pb							
$PbSO_3$ ($P2_1/m$) (scotlandite)	0.0811	0.0849	0.0814	0.0841	0.0870	0.0894	0.0976
$PbSO_3$ (*Pnma*)	0.0809	0.0865	0.0816	0.0849	0.0883	0.0894	0.0976
$PbSeO_3$ (molybdomenite)	0.0807	0.0861	0.0823	0.0843	0.0854	0.0878	0.0945
α-$PbSeO_3$	0.0804	0.0880	0.0837	0.0852	0.0861	0.0884	0.0949
Halogenites							
Ba							
$Ba(ClO_3)_2$	0.0799	0.0838	0.0851	0.0870	0.0874	0.0950	0.0987
$Ba(BrO_3)_2$-I	0.0837	0.0870	0.0851	0.0887	0.0888	0.0960	0.0994
$Ba(BrO_3)_2$-II	0.0797	0.0843	0.0851	0.0860	0.0857	0.0919	0.0947
K							
$KClO_3$	0.0807	0.0849	0.0818	0.0852	0.0876	0.0926	0.1006
$KClO_3$-HT	0.0814	0.0856	0.0811	0.0857	0.0883	0.0934	0.1017
$KClO_3$-HP, LT-II	**0.0788**	0.0829	0.0829	*0.0829*	0.0867	0.0893	0.0990
$KBrO_3$	**0.0788**	0.0830	0.0830	*0.0805*	0.0882	0.0876	0.1019
Na							
$NaClO_3$-I	0.0799	*0.0836*	*0.0823*	0.0851	0.0830	0.0919	0.0946
$NaBrO_3$	0.0796	*0.0843*	*0.0830*	0.0847	0.0819	0.0905	0.0925
$NaIO_3$ ($Pbn2_1$)	**0.0789**	0.0832	0.0833	0.0962	0.0942	0.0943	0.0981
$NaIO_3$ (*Pbnm*)	**0.0788**	0.0831	0.0832	0.0851	0.0813	0.0870	0.0884

the sizes of the L atoms. An inverse tendency is observed only for $Ba(BrO_3)_2$-I. Note that $Ba(BrO_3)_2$-I is likely to be metastable since it is obtained by the reaction

$$Ba(BrO_3)_2{\cdot}H_2O \overset{333-342\,\mathrm{K}}{\longrightarrow} Ba(BrO_3)_2\text{-I},$$

and the structure motif of initial $Ba(BrO_3)_2{\cdot}H_2O$ is preserved in the anhydrous product (Lutz *et al.*, 1990). In some other cases (K_2SO_3–K_2TeO_3 and Na_2SO_3–Na_2SeO_3) the G_3 values are the same with the estimated error.

(ii) Increase of the uniformity leads to a change of the topological motif of an array: it tends to be b.c.c.

(iii) Contrary to an increase of the uniformity of the $\{M,L\}$ array, the uniformity of other ion sublattices decreases (corresponding G_3 values increase). This rule is fulfilled for all compounds, but Mn^{II} salts, and reflects the competition of ion arrays to be structure-forming.

(iv) In the salts with large alkali metals (K, Rb, Cs) or ammonium cations the mixed cation arrays choose the most uniform b.c.c. motif, as a rule. According to Blatov & Zakutkin (2002), this tendency is caused by mainly undirected ion interactions that do not restrict the ion arrangement.

(v) In high-temperature and high-pressure phases the mixed cation arrays additionally decrease their G_3 values because the ambient factors promote an increase of uniformity and symmetry of the structure-forming array. Only in $KClO_3$-HT and $CdSO_3$-III does the $\{M,L\}$ sublattice become slightly less uniform than in the low-temperature phase.

4. Concluding remarks

The crystallochemical analysis of anhydrous salts $M_y(LO_3)_z$ with pyramidal anions LO_3 (L = S, Se, Te, Cl, Br, I) revealed regularities similar to those found recently for salts with triangular (Blatov & Zakutkin, 2002) and tetrahedral oxygen- (Vegas & Jansen, 2002; Ilyushin *et al.*, 2004) and halogen-containing anions (Peskov & Blatov, 2004). The most important manifestations of these regularities are the relationships between almost half (49.2%) the $M_y(LO_3)_z$ substances and A_yX_z compounds at the level of partial isotypism. Analysis of the results obtained for the salts with triangular, pyramidal and tetrahedral anions shows that the NaCl (**pcu-b**) topological motif is the most preferable (Table 9). Besides, the $M_y(LO_3)_z$ salts correspond to the other widespread topological types collected in the RCSR database: **nia**, **scu**, **bnn**, **rtl**.

Considering topology and uniformity of the ion arrays in the $M_y(LO_3)_z$ compounds one can draw the conclusion that the mixed cation arrays $\{M,L\}$ usually have a leading role caused by similar sizes and charges of M and LO_3 ions. Thus, our data confirm the results of O'Keeffe & Hyde (1985), Vegas (2000), Blatov (2001), Vegas & Jansen (2002), Blatov & Zakutkin (2002), Ilyushin *et al.* (2004) and Peskov & Blatov (2004), suggesting a high structure-forming role of cation arrays in inorganic compounds. It is noteworthy that the comparison of binary and ternary compounds gives rise to a new interpretation of the notion *structure-forming array*. This is an array that obeys the two following criteria:

(i) It should be the most uniform, *i.e.* it should have the smallest G_3 value in comparison with other arrays;

(ii) Its topology should tend to one of the widespread topological types of close packings, b.c.c. lattice or other nets, typical for binary compounds.

Table 9
Topological similarities between binary and ternary compounds.

Topological types of the binary compounds of a given stoichiometric composition are arranged according to the number of their relationships with the families of the ternary compounds. The ‘+’ sign means that at least one example of the relationship was found for a given ternary family and a topological type of binary compound.

		CN		Composition of complex anion in ternary compound									
Binary compound	RCSR nomenclature	*A*	*X*	SiO_4^{4-}	GeO_4^{4-}	PO_4^{3-}	AsO_4^{3-}	SO_4^{2-}	SeO_4^{2-}	ClO_4^-	BrO_4^-	IO_4^-	MoO_4^{2-}
AX													
NaCl	**pcu-b**	6	6	–	–	+	–	+	+	+	–	–	+
FeS (NiAs)	**nia**	6	6	–	–	+	+	+	+	–	–	–	–
FeB	–	7	7	–	–	–	–	+	–	+	+	–	–
ZnS (sphalerite)	**dia**	4	4	–	–	+	+	+	–	–	–	–	–
ZnTe (hex BN)	**bnn**	5	5	–	–	+	+	–	–	–	–	–	–
CsCl	**bcu**	8	8	–	–	–	–	–	–	–	–	–	–
PtS	**pts**	4	4	–	–	–	–	+	–	–	–	–	–
CdTe	**qtz**	4	4	–	–	+	+	–	–	–	–	–	–
SnP	**sqp**	5	5	–	–	–	–	–	–	–	–	–	–
AX_2													
BaF_2	–	11	5, 6	+	+	–	–	+	+	–	–	–	–
$TiSi_2$	–	10	5	+	+	–	–	+	+	–	–	–	–
NdS_2 ($MgCu_2$)	**mgc**	12	6	+	+	–	–	–	–	–	–	–	–
CaF_2	**flu**	8	4	–	–	–	–	+	–	–	–	–	–
$PoCl_2$	**scu**	8	4	–	–	–	–	–	–	–	–	–	–
SiO_2 (moganite)	**mog**†	4	2	–	–	–	–	–	–	–	–	–	–
PdF_2 (FeS_2)	**pyr**	6	3	–	–	–	–	–	–	–	–	–	–
$PbCl_2$	–	7	3, 4	–	–	–	–	+	–	–	–	–	–
WGe_2	–	10	5	–	–	–	–	–	–	–	–	–	–
TiO_2 (rutile)	**rtl**	6	3	–	–	–	–	–	–	–	–	–	–
A_2X_2													
Tl_2S_2	–	4, 8	6	–	–	–	–	–	–	–	–	–	–
AX_3													
UCl_3	–	9	3	–	–	–	–	–	–	+	–	–	–
UH_3	–	12	4	–	–	+	+	–	–	–	–	–	–
BiF_3 (gananite)	–	14	4, 6	–	–	–	+	–	–	–	–	–	–
η-Cu_3Sb	–	12	4	–	–	+		–	–	–	–	–	–
ReO_3	**pcu**†	6	2	–	–	–	–	–	–	+	–	–	–
A_2X_3													
Rh_2O_3	**alw**	6	4	–	–	+	–	+	+	–	–	–	+
α-Al_2O_3	**cor**	6	4	–	–	+	–	+	–	–	–	–	–
Rh_3P_2	–	7	4, 5	–	–	–	–	–	–	–	–	–	+
Ho_2C_3	–	9	6	–	–	+	–	–	–	–	–	–	–
A_3X_4													
Th_3P_4	–	8	6	+	+	–	–	–	–	–	–	–	–

		CN		Composition of complex anion in ternary compound									
Binary compound	RCSR nomenclature	*A*	*X*	BO_3^{3-}	CO_3^{2-}	NO_3^-	SO_3^{2-}	SeO_3^{2-}	TeO_3^{2-}	ClO_3^-	BrO_3^-	IO_3^-	$M\mathrm{Hal}_4$
AX													
NaCl	**pcu-b**	6	6	+	+	+	+	+	–	+	+	–	–
FeS (NiAs)	**nia**	6	6	+	+	–	–	+	–	–	–	+	+
FeB	–	7	7	–	–	–	–	–	–	–	–	–	+
ZnS (sphalerite)	**dia**	4	4	–	–	–	–	–	–	–	–	–	+
ZnTe (hex BN)	**bnn**	5	5	–	–	–	–	+	–	–	–	–	–
CsCl	**bcu**	8	8	–	–	+	–	–	–	–	–	–	+
PtS	**pts**	4	4	–	–	–	–	–	–	–	–	–	+
CdTe	**qtz**	4	4	–	–	–	–	–	–	–	–	–	–
SnP	**sqp**	5	5	–	+	–	–	–	–	–	–	–	–
AX_2													
BaF_2	–	11	5, 6	–	+	–	–	–	–	–	–	–	+
$TiSi_2$	–	10	5	–	–	–	–	–	–	–	–	–	–
NdS_2 ($MgCu_2$)	**mgc**	12	6	–	–	–	–	–	–	–	–	–	+
CaF_2	**flu**	8	4	–	+	–	–	–	–	–	–	–	+
$PoCl_2$	**scu**	8	4	–	–	–	–	–	–	–	+	–	+

Table 9 (continued)

		CN		Composition of complex anion in ternary compound									
Binary compound	RCSR nomenclature	A	X	BO_3^{3-}	CO_3^{2-}	NO_3^-	SO_3^{2-}	SeO_3^{2-}	TeO_3^{2-}	ClO_3^-	BrO_3^-	IO_3^-	MHal$_4$
SiO_2 (moganite)	**mog**†	4	2	–	–	+	–	–	–	–	–	–	–
PdF_2 (FeS_2)	**pyr**	6	3	–	–	+	–	–	–	–	–	–	–
$PbCl_2$	–	7	3, 4	–	–	–	–	–	–	–	–	–	–
WGe_2	–	10	5	–	+	–	–	–	–	–	–	–	–
TiO_2 (rutile)	**rtl**	6	3	–	–	–	–	+	–	–	–	–	–
A_2X_2													
Tl_2S_2	–	4, 8	6	–	–	–	–	–	–	+	–	–	–
AX_3													
UCl_3	–	9	3	+	–	–	–	–	–	–	–	–	–
UH_3	–	12	4	–	–	–	–	–	–	–	–	–	–
BiF_3 (gananite)	–	14	4, 6	–	–	–	–	–	–	–	–	–	–
η-Cu_3Sb	–	12	4	–	–	–	–	–	–	–	–	–	–
ReO_3	**pcu**†	6	2	–	–	–	–	–	–	–	–	–	–
A_2X_3													
Rh_2O_3	**alw**	6	4	–	–	–	–	–	–	–	–	–	–
α-Al_2O_3	**cor**	6	4	+	–	–	–	–	–	–	–	–	–
Rh_3P_2	–	7	4, 5	–	–	–	–	–	–	–	–	–	–
Ho_2C_3	–	9	6	–	–	–	–	–	–	–	–	–	–
A_3X_4													
Th_3P_4	–	8	6	–	–	–	–	–	–	–	–	–	–

† The 2-connected nodes (O atoms) are replaced by the edges of the crystal structure graph.

Thus, it is not surprising that the most uniform arrays $\{M,L\}$ conform to quasi-binary representations $M_y[L]_z$ of the $M_y(LO_3)_z$ salts, namely because these representations uncover close relationships between the $M_y(LO_3)_z$ and A_yX_z substances.

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