'Face-to-face' relationships between oxocentred tetrahedra and cation-centred tetrahedral oxyanions in crystal structures of minerals and inorganic compounds

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ABSTRACT

Detailed analysis of the crystal structures of minerals and inorganic compounds containing oxocentred $[OCu_4]$ tetrahedra reveals the following principle for relationships between oxocentred tetrahedra and tetrahedral oxyanions $(T^{n+}O_4)^{-(8-n)}$ with $T = S^{6+}$ or V^{5+}, or triangular pyramidal oxyanions $(SeO_3)^{2-}$ (which may be considered as $(SeO_3E)^{2-}$ tetrahedra assuming the lone pair E of selenium to be a fourth ligand): $(T^{n+}O_4)^{-(8-n)}$ tetrahedra are 'attached' to the oxocentred tetrahedra so that their grounds (O-O-O and Cu-Cu-Cu) are parallel to each other and the mutual orientation is regular (O corners are exactly under Cu corners). We propose to describe these relationships as 'face-to-face', meaning that the oxocentred and cation-centred tetrahedra 'meet' along their 'whole' triangular faces. Geometric characteristics of 'face-to-face' relationships are discussed.

KEYWORDS: oxocentred tetrahedra, cation-centred tetrahedra, oxyanions, crystal structure.

Introduction

WITHIN the past few years, minerals and inorganic compounds containing anion-centred $[XA_4]$ tetrahedra ($X = O^{2-}$, N^{3-}; A = metal) have aroused particular attention due to their interesting crystal chemical features (Lulei *et al.*, 1995; Schleid, 1996; Krivovichev *et al.*, 1998*b*). This interest may be compared with the general increase in the interest in metal-oxide clusters and their role in metal transport in gases and aqueous solutions. As a result of the studies of exhalation products from the Large fissure Tolbachik eruption (Kamchatka peninsula, Russia, 1975–76), a large suite of associated minerals containing oxocentred $[OCu_4]$ tetrahedra was discovered (Filatov *et al.*, 1992). The oxocentred tetrahedra may be considered as one of the strongest sub-units in the structures and their linkage plays a major role in controlling their physical properties and anisotropy. The minerals are formed as a result of fumarolic activity, showing that oxocentred tetrahedra may also exist in fumaroles from other volcanoes, e.g. Vesuvius (Italy) and Isalco (Salvador).

All exhalation minerals containing $[OCu_4]$ tetrahedra can be assigned to the salts with additional oxygen atoms. They usually contain tetrahedral oxyanions $(T^{n+}O_4)^{-(8-n)}$ with $T = S^{6+}$ or V^{5+}, or triangular pyramidal oxyanions $(SeO_3)^{2-}$ (which may be considered to be $(SeO_3E)^{2-}$ tetrahedra, assuming the lone pair E of selenium regarded as a fourth ligand). The crystal chemical analysis of relationships between $[OCu_4]$ tetrahedra and tetrahedral oxyanions reveals one interesting feature to which we pay particular attention in this short paper. It appears that this feature is observed also in minerals of non-exhalational genesis as well as in some synthetic compounds. Both of these provide additional information for the analysis.

Figure 1 shows the relationships between oxocentred tetrahedral units (drawn as light) and tetrahedral oxyanions (dark). The following principle is clearly seen: it looks as if $(T^{n+}O_4)^{-(8-n)}$ tetrahedra are 'attached' to the oxocentred tetrahedra so that their grounds (O-O-O and Cu-Cu-Cu) are parallel to each other and the mutual orientation is regular (O corners are exactly under Cu corners). To identify these
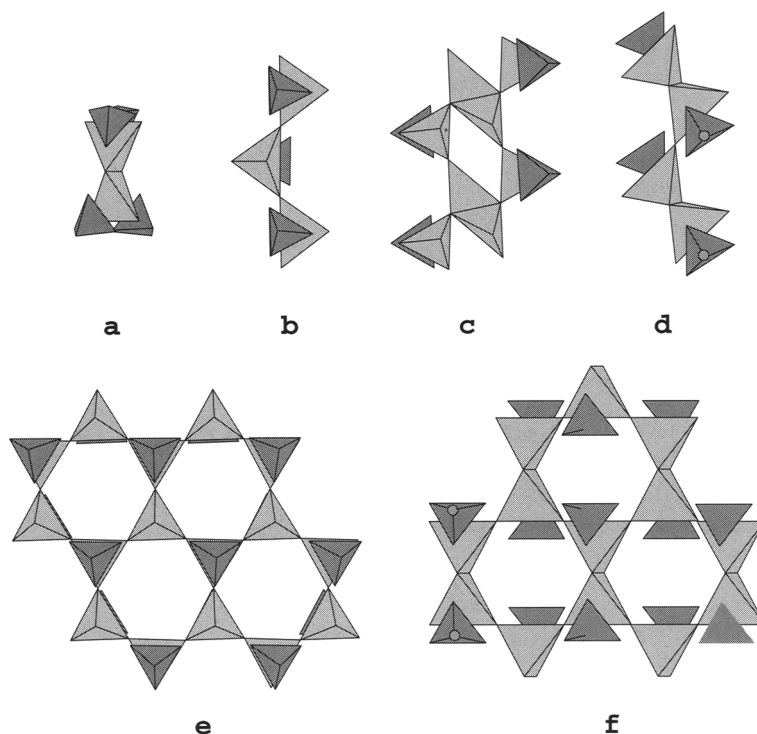
FIG. 1. 'Face-to-face' relationships between oxocentred tetrahedra and cation-centred tetrahedral oxyanions in minerals and inorganic compounds (examples): (a) $[O_2Cu_6]$ double tetrahedra and (SO_4) tetrahedra in fedotovite, $K_2[Cu_3O](SO_4)_3$, and euchlorine, $NaK[Cu_3O](SO_4)_3$; (b) $[O_2Cu_6]$ single chains and (SO_4) tetrahedra in kamchatkite, $K[Cu_3O](SO_4)_2Cl$; (c) $[O_2Cu_5]$ single chains and (SeO_3E) groups in georgbokiite, $[Cu_5O_2](SeO_3)_2Cl_2$; (d) $[O_2Cu_5]$ double chains and (VO_4) groups in stoiberite, $[Cu_5O_2](VO_4)_2$; (e) $[O_2Cu_5]$ layers and (VO_4) groups in averievite, $[Cu_5O_2](VO_4)_2 \cdot MCl$; (f) $[O_2Cu_3Bi]$ layers and (SeO_3E) groups in francisite, $[Cu_3BiO_2](SeO_3)_2Cl_2$ (see detailed refs. in Table 1).

relationships we propose using the term 'face-to-face', taken from the theory of space partitions of Engel (1986). It means that the oxocentred and cation-centred tetrahedra 'meet' along the 'whole' of their triangular faces.

Table 1 gives a survey of inorganic compounds in which a 'face-to-face' relationship exists. Evidently, the length of Cu-Cu edges of $[OCu_4]$ tetrahedra are in the range 3.15−3.25 Å, whereas that of O-O edges of cation-centred tetrahedra have values from approximately 2.4 (sulphates) to 2.5 (phosphates) and 2.6 (selenites) to 2.8 Å (vanadates). However, the mean Cu-O bond lengths which are responsible for the 'face-to-face' relationships (i.e. those of oxocentred tetrahedra) in these structures are approximately the same (1.95−2.03 Å) with the exception of kamchatkite (2.17 Å).

It should be noted that in some minerals and compounds given in Table 1 there are cation-centred tetrahedra not involved in 'face-to-face' relationships (e.g. stoiberite and chloromenite). It is obvious that they are symmetrically independent from those 'attached' to the oxocentred tetrahedra.

It should also be noted that the 'face-to-face' principle does not work in minerals and inorganic compounds with oxocentred tetrahedra built by relatively large metal atoms (Pb or rare earths). In this case the length of metal–metal edges is approximately 3.8−4.0 Å, which is much longer than that of O-O edges in cation-centred tetrahedral groups (in this case Δ = <Cu−Cu>−<O−O> $\gg$ 1 Å). Therefore, this mechanism is appropriate only for compounds with relatively small oxocentred tetrahedra having corresponding edges equal to 3.0−3.3 Å.

TABLE 1. Geometric characteristics of 'face-to-face' relationships between oxocentred [OCu$_4$] tetrahedra and tetrahedral oxyanions [(SO$_4$), (VO$_4$), (SeO$_3$E) where E = lone electron pair] in crystal structures of minerals and inorganic compounds

Mineral	Chemical formula	Type of oxocentred unit	Fig.	<Cu–Cu> [Å]	<O–O> [Å]	Δ [Å]*	<Cu–O> [Å]	Ref.
Fedotovite	K$_2$[Cu$_3$O](SO$_4$)$_3$	Double tetrahedra	1a	3.18	2.42	0.76	1.99	1
Euchlorine	NaK[Cu$_3$O](SO$_4$)$_3$	Double tetrahedra	1a	3.18	2.38	0.80	1.99	2
–	Cu[Cu$_3$O](SeO$_3$)$_3$	Double tetrahedra	1a	3.16	2.62	0.54	1.99	3
–	Cu[Cu$_3$O](SeO$_3$)$_3$	Double tetrahedra	1a	3.19	2.62	0.57	1.99	3
Kamchatkite	K[Cu$_3$O](SO$_4$)$_2$Cl	Single chains	1b	3.17	2.41	0.76	2.17	4
Chloromenite	Cu$_9$[Cu$_6$O$_2$](SeO$_3$)$_4$Cl$_6$	Single chains	1b	3.17	2.60	0.57	1.99	5
Georgbokiite	[Cu$_5$O$_2$](SeO$_3$)$_2$Cl$_2$	Single chains	1c	3.18	2.64	0.54	1.96	6
–	[Cu$_5$O$_2$](PO$_4$)$_2$	Single chains	1c	3.16	2.50	0.66	1.98	7
Stoiberite	[Cu$_5$O$_2$](VO$_4$)$_2$	Double chains	1d	3.15	2.88	0.27	2.03	8
Averievite	[Cu$_5$O$_2$](VO$_4$)$_2$MCl	Layers	1e	3.23	2.83	0.40	2.02	9
–	[Pb$_2$Cu$_8$O$_2$](SeO$_3$)$_2$(NO$_3$)$_2$	Layers	1e	3.23	2.63	0.60	1.96	10
Francisite	[Cu$_3$BiO$_2$](SeO$_3$)$_2$Cl$_2$	Layers	1f	3.23	2.65	0.58	1.96	11
–	[Cu$_3$ErO$_2$](SeO$_3$)$_2$Cl$_2$	Layers	1f	3.17	2.63	0.54	2.01	12

* Δ = <Cu – Cu> . <O– O>

Refs.: [1] Starova et al., 1991; [2] Scordari and Stasi, 1990; [3] Effenberger and Pertlik, 1986; [4] Varaksina et al., 1990; [5] Krivovichev et al., 1998a; [6] Krivovichev et al., 1998b; [7] Brunel-Lauegt and Guitel, 1977; [8] Shannon and Calvo, 1973; [9] Starova et al., 1997; [10] Effenberger, 1986; [11] Pring et al., 1990; [12] Berrigan and Gatehouse, 1996.

The mechanism of the principle considered above can be understood as an accommodation of cation-centred tetrahedra to anion-centred tetrahedral units and may be proposed as the second principle of mutual adaptation between anion-centred polycations and anions of different type and structure. The first principle (adaptation of single chains of edge-sharing anion-centred tetrahedra to the large halide ions) was recently described in Krivovichev and Filatov (1998).

Acknowledgements

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