ELSEVIER

Journal of Alloys and Compounds 281 (1998) 152–156

Journal of ALLOYS AND COMPOUNDS

The Bi(III)-selenite $(Bi_2O)Cu(SeO_3)_3{\cdot}H_2O$

H. Effenberger

Institut für Mineralogie und Kristallographie, Universität Wien, Althanstraße 14, A-1090 Vienna, Austria

Received 28 April 1998; received in revised form 13 July 1998

Abstract

$(Bi_2O)Cu(SeO_3)_3{\cdot}H_2O$ was synthesized under hydrothermal conditions. The crystal structure was determined from single-crystal X-ray diffraction data [$a=11.012(4)$ Å, $b=16.231(6)$ Å, $c=5.640(2)$ Å, space group *Abm*2, $Z=4$, $R1(F)=0.0390$ for 1430 reflections with $F_o>4\sigma(F_o)$ and 84 variable parameters]. The $Bi^{[1+5]}$ atom has one short bond of 2.174(5) Å to an oxo-oxygen atom, the pentagonal–pyramidal coordination figures are edge-connected among each other to form chains. Tetragonal pyramidal $Cu^{[4+1]}O_5$ polyhedra are corner-connected to $^{1}_{\infty}[CuO_3(H_2O)]$ units. Both chains are extended along the *c*-axis and they are linked by the selenite groups. Probable hydrogen bonds are to oxygen atoms of the selenite group, $O_w \cdots O(23)=2.604(13)$ Å, $O(23)\cdots O_w \cdots O(23)=84.6(6)°$. The connection of the Bi atoms and parts of the SeO_3 groups show topological similarities to $Bi_4Cu_3O_6(VO_4)_2$.

Keywords: $(Bi_2O)Cu(SeO_3)_3{\cdot}H_2O$, synthesis; $(Bi_2O)Cu(SeO_3)_3{\cdot}H_2O$, crystal structure; $(Bi_2O)Cu(SeO_3)_3{\cdot}H_2O$, topology; $Bi_4Cu_3O_6(VO_4)_2$, topology

1. Introduction

Bi(III)-selenites are almost unknown. Recently the mineral francisite, $BiCu_3O_2Cl(SeO_3)_2$, was described and structurally characterized from single-crystal X-ray diffraction data [1]. During the study of the system Bi_2O_3–CuO–SeO_2–H_2O, two modifications of $Bi_2Cu(SeO_3)_4$ with the same space-group symmetry but with a different structural topology were isolated [2]. These investigations were continued due to general interest in the stereochemistry of lone-pair elements. The present paper deals with the description of the first hydrated oxo-selenite compound $(Bi_2O)Cu(SeO_3)_3{\cdot}H_2O$. The topological analogy to $Bi_4Cu_3O_6(VO_4)_2$ [3] is discussed.

2. Synthesis and X-ray structure investigation

To synthesize $(Bi_2O)Cu(SeO_3)_3{\cdot}H_2O$ mixtures of Bi_2O_3, CuO and H_2SeO_3 were inserted into teflon-lined steel vessels. The vessels were kept at 503 K for 3 days and then cooled to room-temperature (cooling rate 1 $K\,h^{-1}$). $(Bi_2O)Cu(SeO_3)_3{\cdot}H_2O$ is light-green and pleochroic (light-green to nearly colourless), the orthorhombic bipyramidal crystals are elongated parallel to [001], the morphology is defined by the crystallographic forms {100}, {010} and {001}. Byproducts are $CuSeO_3$-III, $Cu(SeO_3){\cdot}2H_2O$, $Cu(SeO_2OH)_2$, $Cu(Se_2O_5)$, $Cu_2O(SeO_3)$-I and II, $Cu_4O(SeO_3)_3$-II, and $Bi_2Cu(SeO_3)_4$-I and II [2,4–8]. The ratio of the formed compounds changed in different syntheses runs; the huge number of simultaneously obtained phases indicates that at least in parts equilibrium was not reached. Single-crystal chips of $(Bi_2O)Cu(SeO_3)_3{\cdot}H_2O$ were preliminarily investigated by X-ray film methods which gave the Laue symmetry *mmm*, the reflection condition *hkl*: $k+l=2n$ (characteristic for the space groups *Abmm*, *Abm*2, and *Ab*2*m*) and rough cell parameters. Final lattice parameters were calculated by least-squares refinements of accurate determined 2ϑ values measured on a STOE four-circle diffractometer. Crystal data, details on X-ray data collection and results of structure refinement are given in Table 1.

A trial to solve the structure in the centric space group *Abmm* failed. For space group *Abm*2 the atomic coordinates of Bi and Se were derived using a Patterson summation and direct methods. The Cu and O atoms were located by succeeding difference Fourier summations [9,10]. The atomic arrangement clearly shows a polar axis in [001] corresponding to the absence of an inversion centre. As expected, H atoms could not be detected experimentally. The crystal structure was refined on F^2 [10], and neutral-atomic complex scattering functions [11] were used, anisotropic displacement parameters were allowed for all atoms. Final structural parameters are given

0925-8388/98/$ – see front matter
PII: S0925-8388(98)00753-1

Table 1
Details on single-crystal X-ray data collection and structure refinements of $(Bi_2O)Cu(SeO_3)_3 \cdot H_2O$ on a STOE AED 2 four-circle diffractometer (Mo tube, graphite monochromator, corrections for Lorentz and polarization effects)

a	11.012(4) Å
b	16.231(6) Å
c	5.640(2) Å
V	1008.1 $Å^3$
Space group	*Abm*2
Z	4
ρ_{calc}	5.91 g cm^{-3}
Crystal dimensions	$0.03 \times 0.04 \times 0.15$ mm^3
Scan speed ($2\vartheta/\omega$ scan mode)	0.9 to 3.6° min^{-1}
Scan width ($+\alpha_1 - \alpha_2$ dispersion)	1.20°
Maximal variation of intensity	±0.53%; 3 standards, 2 h
Range of data collection	$2° < 2\vartheta < 70°$
μ(Mo Kα)	48 mm^{-1}
Empirical absorption correction	ψ-scans
Transmission factors	0.0230 to 0.0747
Total measured reflection	5163
Unique reflections (n)	2288
Reflections with $F_o > 4\sigma(F_o)$	1430
$R1 = \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma \|F_o\|$	0.0390
$wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$	0.0876
$s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$	0.869
Variable parameters (p)	84
Extinction coefficient	0.00023(5)
Max Δ/σ	≤ 0.001
Flack×parameter	0.018(13)
Final difference Fourier map	-1.58 to $+1.87$ e$Å^{-3}$

$w = 1/\{\sigma^2(F_o^2) + [0.0387*([\max(0, F_o^2)] + 2*F_c^2)/3]^2\}$.

Table 3
Selected interatomic bond distances in $(Bi_2O)Cu(SeO_3)_3 \cdot H_2O$ (in Å)

Bi–O_o	2.174(5)		Cu–O(22)	1.951(8)	2×
Bi–O(21)	2.362(8)		Cu–O(11)	1.967(13)	
Bi–O(21)	2.411(8)		Cu–O_w	1.968(13)	
Bi–O(12)	2.416(8)		Cu–O_w	2.239(13)	
Bi–O(12)	2.464(9)				
Bi–O_o	2.603(7)		Se(1)–O(11)	1.700(14)	
Bi–O(23)	2.881(9)		Se(1)–O(12)	1.710(8)	2×
Bi–O(11)	3.087(6)				
Bi–O(22)	3.520(10)		Se(2)–O(23)	1.674(8)	
			Se(2)–O(22)	1.675(9)	
$O_w \cdots$O(23)	2.604(13)	2×	Se(2)–O(21)	1.739(9)	

in Table 2. Selected bond lengths are compiled in Table 3. The highest peaks in the final difference Fourier map are in the vicinity of the Bi atoms.

3. Results of structure refinements

In $(Bi_2O)Cu(SeO_3)_3 \cdot H_2O$ the nearest and next-nearest neighbour environment of the Bi atom is formed by two oxo-oxygen atoms (Bi–O = 2.174(5) Å and 2.603(7) Å) and four O atoms belonging to selenite groups (Bi–O = 2.362(8) to 2.464(9) Å). The ligands are arranged in a distorted pentagonal pyramid with the shortest bond length towards the apex; the Bi atom is in the centre of the basal plane: the O–Bi–O angles are 71.72(8)° to 97.4(2)° between the apex and the O atoms in the basis, and they vary from 65.0(2)° to 79.8(3)° ($\Sigma_{n=1}^{5} = 365.1°$) for *cis*-

Table 2
Atomic coordinates and equivalent isotropic displacement parameter (in $Å^2$) [12] for $(Bi_2O)Cu(SeO_3)_3 \cdot H_2O$ (e.s.d.'s in parentheses)

Atom	x	y	z	U_{equiv}
Bi	0.12179(6)	0.58340(2)	0.0[a]	0.01815(11)
Cu(1)	0.39624(19)	0.25	0.2569(4)	0.0172(4)
Se(1)	0.11930(19)	0.25	0.0921(3)	0.0151(3)
Se(2)	0.35668(12)	0.07360(6)	0.0317(2)	0.0173(3)
O(11)	0.2205(12)	0.25	0.3197(24)	0.029(3)
O(12)	0.0351(9)	0.3314(5)	0.1922(14)	0.0220(18)
O(21)	0.2280(9)	0.0329(5)	0.1665(15)	0.0208(16)
O(22)	0.4084(9)	0.1301(5)	0.2588(17)	0.0251(19)
O(23)	0.2927(9)	0.1420(5)	−0.1523(17)	0.0253(18)
O_o	0.0	0.0	0.3145(19)	0.021(3)
O_w	0.5659(11)	0.25	0.147(2)	0.017(2)

[a] Fixed for definition of origin.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi	0.01448(16)	0.01771(14)	0.02227(17)	−0.00413(22)	−0.00284(32)	0.00011(19)
Cu(1)	0.0116(12)	0.0173(7)	0.0226(9)	0.0	0.0001(7)	0.0
Se(1)	0.0134(7)	0.0147(6)	0.0172(6)	0.0	−0.0016(9)	0.0
Se(2)	0.0133(6)	0.0152(4)	0.0234(9)	−0.0003(3)	0.0014(5)	−0.0008(4)
O(11)	0.015(6)	0.052(8)	0.022(6)	0.0	0.000(5)	0.0
O(12)	0.022(5)	0.020(4)	0.024(4)	−0.005(3)	−0.005(3)	0.005(3)
O(21)	0.024(4)	0.020(3)	0.019(3)	−0.005(3)	0.002(3)	−0.002(4)
O(22)	0.023(5)	0.021(3)	0.031(4)	0.003(3)	−0.013(4)	−0.006(3)
O(23)	0.018(4)	0.021(4)	0.037(5)	0.007(3)	−0.005(4)	−0.002(3)
O_o	0.025(7)	0.029(6)	0.009(5)	0.0	0.0	−0.004(5)
O_W	0.006(5)	0.017(5)	0.028(6)	0.0	−0.001(5)	0.0

arranged oxygen atoms within the basis. The distances from the least-squares plane $7.53(2)x+9.71(3)y+2.361(9)z=6.209(17)$ (x, y, z in crystal coordinates) are $+0.469(6)$ to $-0.614(5)$ Å for the five O atoms defining the basal plane, 0.370 (4) Å for the Bi atom and $-1.794(5)$ Å for the apex. This one-sided arrangement of the ligands makes allowance for the space requirements of the stereoactivity of the $6s^2$ lone-pair electrons of the Bi(III) atom. The gap to further ligands is 0.28 Å.

The Cu atom has site symmetry m and the common tetragonal pyramidal [4+1] coordination, $\langle$Cu–O$\rangle$ within the basal plane is 1.959 Å, Cu–O to the apex is 2.239(13) Å. The coordination is quite regular, the O–Cu–O angles are 86.4(3)° to 97.6(4)° for neighbouring and 172.0(4)° and 172.1(4)° for *trans*-arranged ligands. Interactions to further ligands are excluded from discussion due to Cu–O$\geq$3.47 Å. The distance of the O atoms from the basal least-squares plane (x, y, z in crystal coordinates) $2.70(5)x+5.468(7)z=2.43(0.02)$ varies from $-0.096(7)$ to $+0.090(7)$ Å, that of the Cu atom is 0.047(7) Å. The apex and one of the ligands within the basal plane are H_2O molecules, the three other ligands belong to selenite groups.

The O_w atom is located at the mirror plane. The probable hydrogen bonds are to two symmetrically restricted O atoms of selenite groups with $O_w \cdots O(23)=2.604(13)$ Å, the small angle $O(23) \cdots O_w \cdots O(23)=84.6(6)°$ indicates moderately bent hydrogen bonds. The O_w atom has an approximately tetrahedral environment by the two hydrogen atoms and by the two Cu atoms (Fig. 1; program ATOMS [13] was used to prepare the figures). Bond valence calculations support the hydrogen bonding scheme (Table 4). The O_w atom needs two covalently bound H atoms to get saturated. The insufficient sum of bond valences reaching the O(23) atom from the Bi and Se atoms indicates that the O(23) is the acceptor of the hydrogen bond. Bond valences are satisfactory for the other oxygen atoms and range from 1.87 to 2.04. The two crystallographically different selenite groups have symmetry m and 1, respectively. The average $\langle$Se–O$\rangle$ bond distances are 1.707 and 1.696 Å, O–Se–O angles are 96.1(4) to 104.7(4)°.

The $Bi^{[1+5]}O_6$ coordination figures share edges to form chains parallel to [001]. Considering only the O_o ligands $[Bi_2O]$ chains are formed. The O_o atoms are located at the two-fold axis, but the $[Bi_2O]$ chains have *pseudo*symmetry 4_2. Including next-nearest ligands the one-dimensional structural unit is maintained (Fig. 2(a)). The O_o atoms are surrounded by a strongly distorted tetrahedron of Bi atoms with two short and two long O_o–Bi bonds. The Bi–O_o–Bi bond angle is increased between the two short O_o–Bi bonds to 122.5(5)° and it is decreased to 94.1(3)° between the two long O_o–Bi bonds. The four other angles are close to those in a regular tetrahedron: 108.8(1) and 109.5(1)°. A slight shift of the O_o atom towards to $z=\frac{1}{4}$ would enable a more balanced coordination around both the O_o and the Bi atoms. Four-coordinated oxo-oxygen atoms, neither belonging to an anion group nor acting as a donor or acceptor of a hydrogen bond, are common in inorganic compounds. The OM_4 environments sometimes are distorted for M=Bi; in contrast, the OM_4 tetrahedron is rather regular for M=first row transition elements; the distortion seems to be correlated with the coordination numbers, the ionic radii and the valence states of the M atoms.

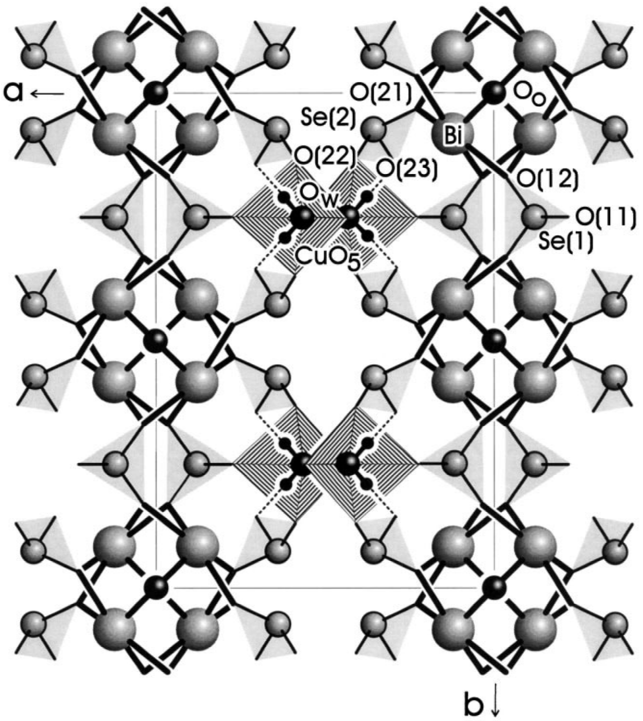

Fig. 1. The crystal structure of $(Bi_2O)Cu(SeO_3)_3 \cdot H_2O$ in a projection on (001).

The CuO_5 polyhedra share corners to form chains parallel to [001] (Fig. 2(b)). The $[Bi_2O]$ chains are connected by the $Se(1)O_3$ groups to layers along (100).

Table 4
Bond valences (in valence units) calculated according to Ref. [14]. The arrows indicate the multiplicity of contributions to the sum of bond valences

	Bi	Cu	Se(1)	Se(2)	$\Sigma\nu$ (excluding H)
O(11)	0.06↓→	0.46↓→	1.35↓→		1.87
O(12)	0.38↓→ 0.34↓→		1.31↓↓→		2.03
O(21)	0.44↓→ 0.39↓→			1.21↓→	2.04
O(22)		0.48↓↓→		1.44↓→	1.92
O(23)	0.11↓→			1.45↓→	1.56
O_o	0.73↓→→ 0.23↓→→				1.92
O_w		0.46↓→ 0.22↓→			0.68
$\Sigma\nu$	2.68	2.10	3.97	4.10	

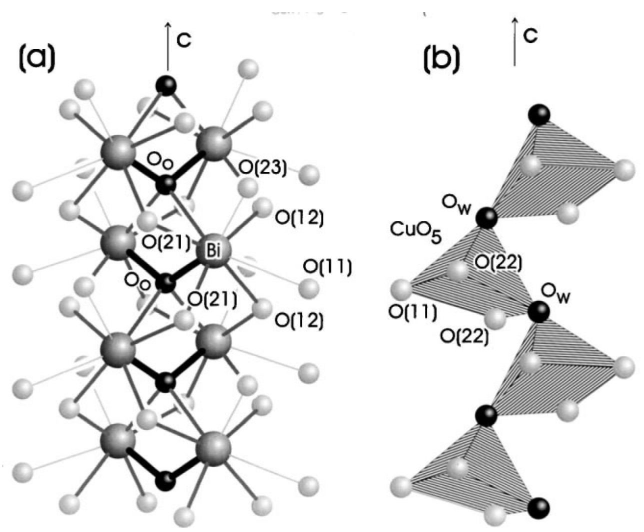

Fig. 2. Detail of the crystal structure of $(Bi_2O)Cu(SeO_3)_3 \cdot H_2O$; (a) the connection of the coordination polyhedra around the Bi atoms parallel to [001]; (b) the connection of the tetragonal pyramidal CuO_5 coordination figures parallel to [001].

$Se(2)O_3$ groups are branched parallel to [100], and they link to the CuO_5 polyhedra. The largest anisotropies of the principal mean-square atomic displacements were observed for the low coordinated oxygen atoms O(11): 0.052, 0.022, 0.015 Å^2, O(22): 0.042, 0.020, 0.013 Å^2 and O(23): 0.041, 0.018, 0.017 Å^2.

Structurally related to $(Bi_2O)Cu(SeO_3)_3 \cdot H_2O$ is the compound $Bi_4Cu_3O_6(VO_4)_2$ [3]. The $Bi_2^{[4+6]}O$ chains and their connection by VO_4 tetrahedra in (001) are topologically comparable to the Bi–SeO_3 layers in (100) of the title compound (Fig. 3). However, the coordination of the central oxo-oxygen atom is more regular in the vanadate with the O_o–Bi bonds being 2.243 to 2.351 Å, and the Bi–O_o–Bi angles ranging from 107.0(5) to 111.2(5)°. The two type structures differ mainly in the connection of the layers. In $Bi_4Cu_3O_6(VO_4)_2$, ribbons formed by corner-connected CuO_4 squares run parallel to [100]. The ribbon is centered between two Bi-chains with an additional oxo-oxygen atom coordinated to two Cu and two Bi atoms. In the title compound a chain formed by the CuO_5 polyhedra, the $Se(2)O_3$ groups and the hydrogen bonds of the H_2O molecules is the connecting unit centered between four Bi_2O chains. The cell parameter in the direction of the $[Bi_2O]$ chains [$(Bi_2O)Cu(SeO_3)_3 \cdot H_2O$: 5.640(2) Å, $Bi_4Cu_3O_6(VO_4)_2$: 5.317(2) Å] reflects these different structural features.

The three other known Bi–Cu-selenites show similarities with respect to the individual coordination polyhedra but they feature topologically distinct connections. In the two $Bi_2Cu(SeO_3)_4$ modifications $Bi_2(SeO_3)_2$ layers are separated by $Cu(SeO_3)_2$ chains and $Cu(SeO_3)_2$ layers, respectively. The atomic arrangement in francisite consists of an infinite, three-dimensional framework of Bi, Cu, Se and O atoms, with Cl atoms located within channels. Furthermore, the oxo-oxygen atoms are connected to three Cu atoms and to one Bi atom, while the Bi coordination polyhedra are not linked to each other. For a further discussion of $[BiO_2]$ and $[Bi_2O_2]$ layers see Ref. [15].

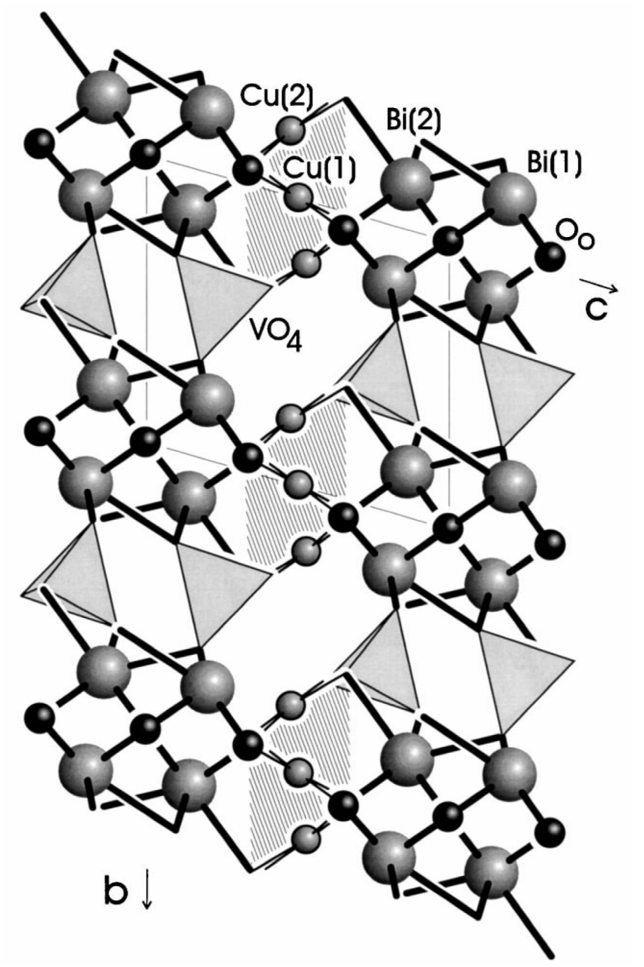

Fig. 3. The crystal structure of $Bi_4Cu_3O_6(VO_4)_2$ [3] in a projection on (100).

Acknowledgements

Financial support by JCPDS/ICDD, Newton Square, PA, USA, is gratefully acknowledged. Comments and suggestions from two anonymous reviewers were greatly appreciated.

References

[1] A. Pring, B.M. Gatehouse, W.D. Birch, Am. Mineral 75 (1990) 1421.
[2] H. Effenberger, Acta Chem. Scand. 50 (1996) 967.
[3] G.B. Deacon, B.M. Gatehouse, G.N. Ward, Acta Crystallogr. C 50 (1994) 1178.
[4] H. Effenberger, Z. Kristallogr. 175 (1986) 61.

[5] P.D. Robinson, P.K.S. Gupta, G.H. Swihart, L. Houk, Am. Mineral 77 (1992) 834.
[6] H. Effenberger, Z. Kristallogr. 173 (1985) 267.
[7] G. Meunier, C. Svensson, A. Carpy, Acta Crystallogr. B 32 (1976) 2664.
[8] H. Effenberger, F. Pertlik, Monatsh. Chem. 117 (1986) 887.
[9] T. Debaerdemaeker, G. Germain, S.E. Hull, M. Irwin, P. Main, C. Tate, M. Woolfson, MULTAN86, Computer programs for the automatic solution of crystal structures from X-ray diffraction data, University of York, UK, 1986.
[10] G.M. Sheldrick, SHELXL-93 Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.
[11] A.J.C. Wilson, (Ed.), International Tables for Crystallography, Vol. C, Kluwer, Dordrecht, 1992.
[12] R.X. Fischer, E. Tillmanns, Acta Crystallogr. C 44 (1988) 775.
[13] E. Dowty, ATOMS 3.2, A Computer Program for Displaying Atomic Structures, Kingsport, TN 37663, 1995.
[14] N.E. Brese, M. O'Keeffe, Acta Crystallogr. B 47 (1991) 192.
[15] R. Enjalbert, S. Sorokina, A. Castro, J. Galy, Acta Chem. Scand. 49 (1995) 813.