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The Covert Water in the Structure of $Sr(ReO_4)_2.2H_2O$: a Revision of the Sesquihydrate Model

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Abstract

The structure of hydrated strontium perrhenate previously reported by Varfolomeev, Samarj, Fuchs & Lunk [*J. Alloy. Compd.* (1993), **201**, 261–265] as the sesquihydrate has been redetermined. A crystal-chemical analysis discloses that the composition of this particular compound obtained in identical crystallization conditions is $Sr(ReO_4)_2.2H_2O$ {strontium bis[tetraoxorhenate(1−)] dihydrate}. The structure contains two independent formula units and one disordered ReO_4 group. This disordered group has the form of a trigonal bipyramid with three essentially ordered equatorial O atoms and two partially occupied Re positions (with site occupancies of 0.58 and 0.42) at the tetrahedron centres. The corresponding axial sites are occupied simultaneously by O atoms (with site occupancies of 0.58 and 0.42) and water molecules (complementing the unit occupancies). The crystallographic evidence for the existence of strontium perrhenate dihydrate is supported by the results of thermal analysis.

Comment

The preparation, stability, composition and analysis of crystal structures of hydrated perrhenates of large divalent metal ions have been the fields of our interest in recent years (Todorov & Macíček, 1995, and references therein). Strontium perrhenate has been reported to crystallize from water in ambient conditions in the form of a dihydrate (Wilke-Dorfurt & Gunzert, 1933). The dihydrate composition has been supported by Smith & Maxwell (1951) (henceforth SM) by thermal analysis; the experimental value of 5.65 wt% loss of water after complete dehydration of the hydrated salt was compared with the calculated value of 5.79 wt% for $Sr(ReO_4)_2.2H_2O$. This formula has also been adopted by Ghosh & Nag (1987). In the course of a preliminary X-ray diffraction study of strontium perrhenate crystals, Varfolomeev, Chupakhin & Plyuschtev (1969) determined an experimental density of 4.52 $Mg\,m^{-3}$, which is in good agreement with $D_x = 4.50$ $Mg\,m^{-3}$ calculated for eight $Sr(ReO_4)_2.2H_2O$ units in a monoclinic cell with $a = 13.266(5)$, $b = 10.14(5)$, $c = 13.608(5)$ Å, $\beta = 92.35(5)°$. Recently, however, Varfolomeev, Samarj, Fuchs & Lunk (1993) (henceforth VSFL) arrived at the conclusion that this salt is a sesquihydrate. This reformulated composition was proposed from a modest-quality X-ray single-crystal structure model [$R = 0.100$, $wR = 0.118$, 3435 reflections with $I > 2\sigma(I)$] in the presence of one atypically disordered ReO_4 group. The large difference between the calculated water content of $Sr(ReO_4)_2.1.5H_2O$ (4.39 wt%) and the experimental value reported by SM (5.65 wt%) was explained by the authors simply in terms of the hygroscopic properties of the hydrated salt.

Before the structural study by Varfolomeev, Samarj, Fuchs & Lunk (1993) was published, the X-ray powder pattern of $Sr(ReO_4)_2.2H_2O$ had been included in the Powder Diffraction File (PDF 42-683; International Center for Diffraction Data, 1992). The close resemblance of the lattice parameters and intensity distribution in the experimental and calculated powder patterns made it clear that these described the same phase. Thus a precise determination of the sample composition was necessary. The thermal analysis and X-ray structure reexamination described here was undertaken with just this aim.

A series of carefully conducted STA (simultaneous thermal analysis) experiments on crystals of hydrated strontium perrhenate, freshly prepared at room temperature and separated from the mother liquor by filtration, repeatedly showed that the dehydration process passed through two stages. The first endothermic effect occurred across the temperature interval 298–358 K and corresponded to a weight loss of 2.81 wt%. Similarly, the second effect occurred between 388 and 437 K and corresponded to a further weight loss of 2.86 wt%, giving a total weight loss of 5.67 wt%. The experimental curve is very close to that reported by SM and corresponds well to the formula $Sr(ReO_4)_2.2H_2O$. The difference of approximately 0.1 wt% is due to the dehydration process, which starts with the separation of crystals from their mother liquor and continues as the crystals are ground. Thus, the thermoanalytical data strongly support the dihydrate formula.

The main features of the structure, shown in Fig. 1, resemble the results obtained by VSFL. Hence, in the present investigation, we follow the numbering scheme adopted by these authors.

Each of the non-equivalent Sr atoms is surrounded by nine O atoms. The coordination polyhedron of

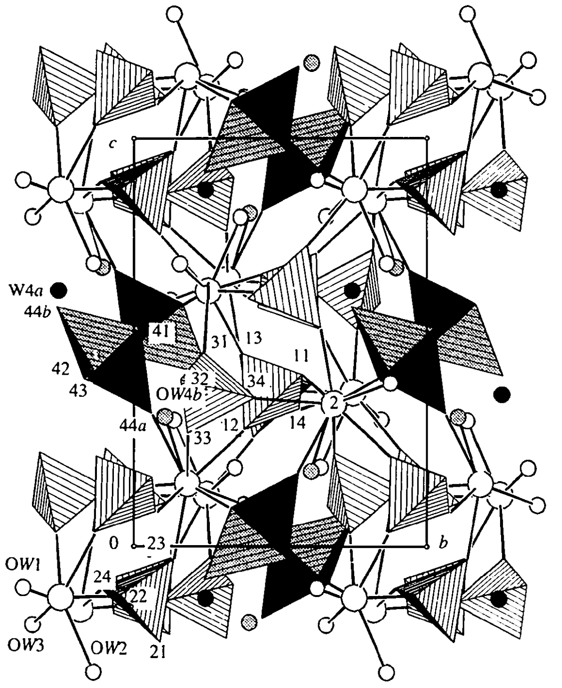

Fig. 1. $Sr(ReO_4)_2.2H_2O$ projected down the *a* axis. The one-digit numbers denote Sr atoms and two-digit numbers are O atoms. The half-shaded trigonal bipyramids illustrate the disordered $Re4O_4$ tetrahedron.

Sr1 is formed by corners pertaining to different Re–O tetrahedra and two water molecules, O*W*2 and O*W*3. The Sr1—O distances range from 2.543 (10) to 2.816 (11) Å, with a mean of 2.645 (10) Å. After Robertson (1977), this polyhedron may be described as a distorted tricapped trigonal prism with O42, O*W*2 and O31 as capping atoms. The O-atom environment of Sr2 has the shape of a distorted monocapped square antiprism (Robertson, 1977) with O11 as the capping atom. The Sr2—O distances vary from 2.583 (9) to 2.729 (11) Å. This polyhedron consists of seven O atoms from seven ReO_4 tetrahedra, O*W*1 and the O44*a*/O*Wb* disordered atoms. When O44*a* is considered the mean Sr—O value is 2.638 (11) Å, and if O*Wb* is considered the mean is 2.642 (12) Å.

The Re atoms are surrounded by O atoms in the form of a relatively regular tetrahedron. In the case of Re1, Re2 and Re3, the Re—O distances and O—Re—O angles fall within the ranges 1.689 (11)–1.747 (9) Å and 107.7 (5)–110.8 (5)°, with mean values of 1.718 (10) Å and 109.5 (5)°, respectively. The corresponding mean values for the Re4*a* and Re4*b* tetrahedra are 1.755 (15) Å and 109.2 (7)°. The individual distances and angles are, however, more scattered [1.678 (9)–1.856 (11) Å, 98.1 (5)–121.4 (7)°]. All O atoms are coordinated to Sr atoms except O32 and O44*b*/O*Wa*.

The disordered motif, represented by a trigonal bipyramid with all important connecting or hydrogen-bonded atoms, is shown in Fig. 2. The two alternative tetrahedron/water orientations are well valence matched (Table 4). This explains the relative stability of $Sr(ReO_4)_2.2H_2O$ crystals. However, to understand why the tetrahedral orientation distribution is 58:42 instead of 50:50 we should consider the structure at a quantum-chemical level.

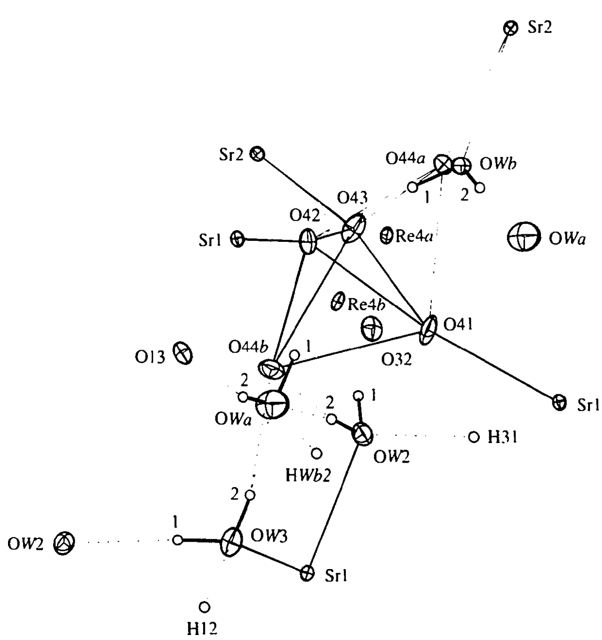

Fig. 2. Disposition of the disordered $Re4O_4$ and water moieties within the surrounding environment of Sr cations and water molecules. The occupancy of atom sites labelled with suffix *a* and *b* are 0.58 and 0.42, respectively. Hydrogen bonds are denoted by dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

The uncoordinated O44*b*/O*Wa* atoms play an accepting role in three weak hydrogen bonds. Although water O atoms usually have a tetrahedral environment, the present linking scheme is possible with the participation of H or alkali metal atoms (Ferraris & Franchini-Angela, 1972) and according to the classification of the same authors it belongs to Class 3. Accordingly, O*W*1 and O*Wb* belong to Class 1 whilst O*W*2 and O*W*3 are of Class 2 (Ferraris & Franchini-Angela, 1972; Chiari & Ferraris, 1982). The O*Wa* molecule is an interstitial species, like the O*W*4 molecule in the structure of $Ba(ReO_4).4H_2O$ (Macíček & Todorov, 1992).

Experimental

Crystals of strontium perrhenate dihydrate were prepared according to Smith & Maxwell (1951). The simultaneous thermal analysis (STA) of a freshly prepared crystalline sample ground to powder (static air, ramp rate 10 K min^{-1}) was carried out using Stanton–Redcroft STA 781 equipment. The weight losses were calculated as percentage lightening of the hydrated salt.

Crystal data

$Sr(ReO_4)_2.2H_2O$
$M_r = 624.04$
Monoclinic
$P2_1/n$
$a = 13.298\,(2)$ Å
$b = 10.080\,(2)$ Å
$c = 13.637\,(4)$ Å
$\beta = 92.39\,(2)°$
$V = 1826\,(1)$ Å^3
$Z = 8$
$D_x = 4.538$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 20.03–21.91°$
$\mu = 32.49$ mm^{-1}
$T = 292$ K
Prismatic
0.06 × 0.06 × 0.06 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Continuous scan profiles
Absorption correction: ψ scan and spherical
$T_{\min} = 0.184$, $T_{\max} = 0.235$
11 043 measured reflections
5311 independent reflections

3506 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.048$
$\theta_{\max} = 30.0°$
$h = 0 \rightarrow 18$
$k = -14 \rightarrow 14$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity decay: 2.7%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.050$
$S = 0.808$
3506 reflections
77 parameters
H atoms refined as riding
$w = 1/[\sigma^2(F) + (0.040F)^2]$

$(\Delta/\sigma)_{\max} = 0.323$
$\Delta\rho_{\max} = 1.61$ e Å^{-3}
$\Delta\rho_{\min} = -5.54$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SDP*/*PDP* (Enraf–Nonius, 1985)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Sr1	0.13910 (8)	0.24742 (10)	0.12510 (8)	0.0120 (2)
Sr2	0.64069 (8)	0.18172 (10)	0.15329 (8)	0.0120 (2)
Re1	0.59602 (4)	0.47262 (5)	0.37469 (3)	0.0115 (1)
Re2	0.37207 (3)	−0.02032 (5)	0.12447 (3)	0.0108 (1)
Re3	0.85203 (4)	0.24996 (5)	0.37726 (4)	0.0159 (1)
Re4*a*†	0.86721 (6)	0.45519 (9)	0.08630 (6)	0.0134 (2)
Re4*b*‡	0.85231 (9)	0.36310 (10)	0.00114 (9)	0.0145 (2)
O11	0.6918 (7)	0.5743 (10)	0.4165 (7)	0.027 (2)
O12	0.6388 (7)	0.3772 (10)	0.2821 (6)	0.026 (2)
O13	0.5604 (7)	0.3695 (10)	0.4679 (7)	0.025 (2)
O14	0.4936 (7)	0.5646 (10)	0.3324 (7)	0.025 (2)
O21	0.4003 (7)	−0.0930 (11)	0.2373 (7)	0.030 (2)
O22	0.2520 (7)	0.0414 (10)	0.1212 (7)	0.026 (2)
O23	0.3811 (7)	−0.1371 (10)	0.0329 (7)	0.028 (2)
O24	0.4536 (7)	0.1094 (10)	0.1054 (8)	0.031 (3)
O31	0.7728 (8)	0.2394 (12)	0.4707 (8)	0.038 (3)
O32	0.9620 (7)	0.1603 (9)	0.4050 (7)	0.028 (2)
O33	0.7977 (7)	0.1850 (10)	0.2718 (7)	0.035 (3)
O34	0.8822 (7)	0.4132 (11)	0.3599 (7)	0.035 (3)
O41	0.8687 (8)	0.5252 (10)	−0.0329 (8)	0.037 (3)
O42	0.9523 (6)	0.3323 (9)	0.0919 (7)	0.027 (2)
O43	0.7437 (8)	0.3699 (13)	0.0732 (9)	0.060 (3)
O44*a*†	0.8920 (13)	0.5693 (17)	0.1780 (12)	0.032 (4)
O44*b*‡	0.859 (2)	0.245 (3)	−0.0883 (19)	0.053 (8)
O*W*1	0.5146 (6)	0.3752 (8)	0.1016 (7)	0.025 (2)
O*W*2	0.1713 (7)	0.1362 (10)	0.3064 (7)	0.034 (3)
O*W*3	0.3135 (6)	0.3422 (10)	0.1909 (8)	0.035 (3)
O*Wa*†	0.8612 (17)	0.241 (3)	−0.1259 (16)	0.086 (8)
O*Wb*‡	0.9466 (19)	0.611 (3)	0.1832 (17)	0.038 (6)

† Site occupancy 0.577. ‡ Site occupancy 0.423.

Table 2. *Selected geometric parameters (Å, °)*

Sr1—O13$^{\rm i}$	2.625 (9)	Re1—O12	1.704 (9)
Sr1—O14$^{\rm ii}$	2.633 (10)	Re1—O13	1.724 (9)
Sr1—O21$^{\rm iii}$	2.543 (10)	Re1—O14	1.727 (9)
Sr1—O22	2.565 (10)	Re2—O21	1.731 (9)
Sr1—O31$^{\rm i}$	2.816 (11)	Re2—O22	1.712 (10)
Sr1—O41$^{\rm iv}$	2.614 (10)	Re2—O23	1.724 (10)
Sr1—O42$^{\rm v}$	2.648 (9)	Re2—O24	1.725 (10)
Sr1—O*W*2	2.733 (10)	Re3—O31	1.689 (11)
Sr1—O*W*3	2.631 (9)	Re3—O32	1.747 (9)
Sr2—O11$^{\rm vi}$	2.686 (10)	Re3—O33	1.712 (10)
Sr2—O12	2.640 (10)	Re3—O34	1.712 (11)
Sr2—O23$^{\rm vii}$	2.583 (9)	Re4*a*—O41	1.773 (11)
Sr2—O24	2.648 (10)	Re4*a*—O42	1.678 (9)
Sr2—O33	2.587 (9)	Re4*a*—O43	1.856 (11)
Sr2—O34$^{\rm vi}$	2.729 (11)	Re4*a*—O44*a*	1.721 (17)
Sr2—O43	2.606 (12)	Re4*b*—O41	1.715 (10)
Sr2—O*W*1	2.647 (9)	Re4*b*—O42	1.806 (9)
Sr2—O44*a*$^{\rm vi}$	2.617 (16)	Re4*b*—O43	1.783 (12)
Sr2—O*Wb*$^{\rm vi}$	2.65 (2)	Re4*b*—O44*b*	1.706 (3)
Re1—O11	1.714 (9)		
O11—Re1—O12	108.6 (5)	O32—Re3—O33	107.7 (5)
O11—Re1—O13	109.8 (4)	O32—Re3—O34	109.2 (5)
O11—Re1—O14	110.8 (5)	O33—Re3—O34	110.1 (5)
O12—Re1—O13	108.5 (5)	O41—Re4*a*—O42	107.6 (5)
O12—Re1—O14	109.8 (4)	O41—Re4*a*—O43	98.1 (5)
O13—Re1—O14	109.4 (4)	O41—Re4*a*—O44*a*	113.0 (7)
O21—Re2—O22	110.1 (5)	O42—Re4*a*—O43	104.8 (5)
O21—Re2—O23	109.6 (5)	O42—Re4*a*—O44*a*	110.6 (6)
O21—Re2—O24	109.9 (5)	O43—Re4*a*—O44*a*	121.4 (7)
O22—Re2—O23	108.8 (5)	O41—Re4*b*—O42	104.5 (5)
O22—Re2—O24	108.2 (5)	O41—Re4*b*—O43	103.2 (6)
O23—Re2—O24	110.2 (5)	O41—Re4*b*—O44*b*	117 (1)
O31—Re3—O32	110.3 (5)	O42—Re4*b*—O43	102.7 (5)
O31—Re3—O33	110.8 (5)	O42—Re4*b*—O44*b*	108 (1)
O31—Re3—O34	108.8 (5)	O43—Re4*b*—O44*b*	119 (1)

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1-x, 1-y, -z$; (v) $x-1, y, z$; (vi) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vii) $1-x, -y, -z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H11···O32$^{\rm i}$	0.95	1.83 (1)	2.77 (1)	168 (1)
O*W*1—H12···O*W*3	0.95	2.05 (1)	3.00 (1)	178 (1)
O*W*2—H21···O32$^{\rm ii}$	0.95	2.22 (1)	3.15 (1)	164 (1)
O*W*2—H22···O*Wa*$^{\rm iii}$	0.95	1.98 (2)	2.93 (3)	171 (1)
···O44*b*$^{\rm iii}$		2.12 (2)	3.06 (3)	172 (1)
O*W*3—H31···O*W*2$^{\rm iv}$	0.95	2.02 (1)	2.97 (1)	177 (1)
O*W*3—H32···O*Wa*$^{\rm iii}$	0.95	1.74 (2)	2.69 (2)	172 (1)
···O44*b*$^{\rm iii}$		2.23 (3)	3.17 (3)	169 (1)
O*Wa*—H*Wa*1···O43	0.95	2.49 (1)	3.44 (3)	179 (1)
O*Wa*—H*Wa*2···O13$^{\rm v}$	0.95	2.16 (1)	3.10 (3)	168 (1)
O*Wb*—H*Wb*1···O42	0.95	2.13 (1)	3.07 (3)	178 (2)
O*Wb*—H*Wb*2···O*Wa*$^{\rm vi}$	0.95	2.14 (2)	3.09 (3)	179 (2)
···O44*b*$^{\rm vi}$		2.35 (3)	3.28 (3)	168 (2)

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $x-1, y, z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $2-x, 1-y, -z$.

Table 4. *Distribution of bond valences*

The bond-valence parameter, r_o, in formula (2) of Brown & Altermatt (1985) was 2.060 Å for Sr—O and 1.929 Å for Re—O; B = 0.37.

	Sr1	Sr2	Re1	Re2	Re3	Re4*a*	Re4*b*	H11	H12	H21	H22	H31	H32	H*Wa*1	H*Wa*2	H*Wb*1	H*Wb*2	$\Sigma(-)$
O11	–	0.18	1.79	–	–	–	–	–	–	–	–	–	–	–	–	–	–	1.97
O12	–	0.21	1.84	–	–	–	–	–	–	–	–	–	–	–	–	–	–	2.05
O13	0.22	–	1.74	–	–	–	–	–	–	–	–	–	–	–	0.12	–	–	2.08
O14	0.21	–	1.73	–	–	–	–	–	–	–	–	–	–	–	–	–	–	1.94
O21	0.27	–	–	1.71	–	–	–	–	–	–	–	–	–	–	–	–	–	1.98
O22	0.26	–	–	1.80	–	–	–	–	–	–	–	–	–	–	–	–	–	2.06
O23	–	0.24	–	1.74	–	–	–	–	–	–	–	–	–	–	–	–	–	1.98
O24	–	0.20	–	1.74	–	–	–	–	–	–	–	–	–	–	–	–	–	1.94
O31	0.13	–	–	–	1.91	–	–	–	–	–	–	–	–	–	–	–	–	2.04
O32	–	–	–	–	1.64	–	–	0.2	–	0.2	–	–	–	–	–	–	–	2.04
O33	–	0.24	–	–	1.80	–	–	–	–	–	–	–	–	–	–	–	–	2.04
O34	–	0.16	–	–	1.80	–	–	–	–	–	–	–	–	–	–	–	–	1.96
O41	0.22	–	–	–	–	0.88	0.75	–	–	–	–	–	–	–	–	–	–	1.85
O42	0.20	–	–	–	–	1.14	0.59	–	–	–	–	–	–	–	–	0.08	–	2.01
O43	–	0.23	–	–	–	0.70	0.63	–	–	–	–	–	–	0.12	–	–	–	1.68
O44*a*†	–	0.13	–	–	–	1.02	–	–	–	–	–	–	–	–	–	–	–	1.15
O44*b*	–	–	–	–	–	–	0.77	–	–	–	0.12	–	0.12	–	–	–	0.08	1.09
O*W*1	–	0.20	–	–	–	–	–	0.8	0.8	–	–	–	–	–	–	–	–	1.80
O*W*2	0.16	–	–	–	–	–	–	–	–	0.8	0.8	0.2	–	–	–	–	–	1.96
O*W*3	0.21	–	–	–	–	–	–	–	0.2	–	–	0.8	0.8	–	–	–	–	2.01
O*Wa*	–	–	–	–	–	–	–	–	–	–	0.12	–	0.12	0.8	0.8	–	0.08	1.92
O*Wb*	–	0.08	–	–	–	–	–	–	–	–	–	–	–	–	–	0.8	0.8	1.69
$\Sigma(+)$	1.88	1.88	7.10	6.99	7.15	3.74	2.74	1.0	1.0	1.0	1.04	1.0	1.04	0.92	0.92	0.88	0.96	–

† The valences of bonds to the disordered atoms were multiplied by the corresponding site occupancy (see Table 1). For the O—H and O···H bonds, valences of 0.80 and 0.20 v.u. were accepted according to Brown (1980).

A well shaped crystal selected from the mother liquor was quickly covered in epoxy resin to prevent dehydration and fixed to the top of a capillary. The positions of the Sr and Re atoms were revealed by direct methods using *SHELXS*86 (Sheldrick, 1985). The initial model was refined and one of the four independent Re atoms was split into Re4*a* and Re4*b*. The occupancy (μ) of Re4*a* refined to 0.577 (1) with the application of the constraint μ(Re4*b*) = $1-\mu$(Re4*a*). The O atoms were found from successive $\Delta\rho$ maps. The intensities were treated for absorption by subsequent application of empirical (based on ψ scans; North, Phillips & Mathews, 1968) and spherical correction routines (Enraf–Nonius, 1988). In the final stage of refinement, all non-H atoms were treated anisotropically. The H atoms were located approximately from $\Delta\rho$ maps at geometrically reasonable positions, checked by *FINDH* (Macíček, unpublished program) and refined as riding on the corresponding O*W* atoms with fixed isotropic displacement factors. The maximum and minimum peaks in the final difference Fourier map are at 0.80 Å from O33 and 0.29 Å from Re3, respectively.

In the process of the structure elucidation and search for the 'missing' water molecule, we paid special attention to the region around the split Re4 atom. The trigonal bipyramidal model of two face-sharing disordered ReO_4 tetrahedra suggested by VSFL was confirmed and further employed. After several trial refinements, we noted that the isotropic displacement factors of the axial O atoms, O44*a* and O44*b*, assuming full site occupancies, exhibited large values ($B_{iso} < 7.5$ Å^2) compared to those of the common-face atoms O41, O42 and O43 ($B < 4.0$ Å^2). Since no peaks in the other geometrically admissible regions of the structure could be extracted from $\Delta\rho$ maps, we considered this to be an artefact from the unsatisfactory absorption correction. The geometry analysis showed that the O44*b* atom was at a distance of 3.18 (3) Å from Re4*a* and 2.85 (3)–3.78 (3) Å from the facial O atoms. Similarly, on the opposite side of the bipyramid, the distances O44*a*···O varied within 2.79 (2)–3.89 (3) Å and the closest Sr and Re4*b* neighbours of O44*a* were at 2.62 (2) and 3.21 (2) Å, respectively. It was suggested that the axial sites are filled in part by a disordered perrhenate O atom [μ(O44*a*) = 0.58, μ(O44*b*) = 0.42] and complemented by one water molecule [μ(O*Wb*) = 0.42, μ(O*Wa*) = 0.58]. This hypothesis proved felicitous and made it possible to refine the final structure to a reliable model.

Data collection: *CAD*-4 (Enraf–Nonius, 1988). Data reduction: *SDP*/*PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SDP*/*PDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992; unpublished).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1122). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Novel Intermetallic Compound, $CeCu_{1-x}Bi_2$

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Abstract

A novel intermetallic compound, $CeCu_{1-x}Bi_2$ ($x = 0.3$) [bismuth–cerium–copper (2/1/0.7)], has been synthesized by the bismuth self-flux method and its structure has been analyzed by single-crystal X-ray diffraction. The compound is found to have the $ZrCuSi_2$ structure type. This can be described as a layered structure in which two-dimensional Bi layers consisting of closely arranged Bi atoms in a square-lattice array and CeBiCu slabs formed by edge-sharing $CeBiCu_4$ distorted octahedra stack alternately along the [001] direction *via* Ce—Bi and Bi—Bi bonds, forming a three-dimensional network.

Comment

Recently, our search for strongly correlated electron systems has concentrated on the synthesis and growth of single crystals of ternary compounds in Ce–*T*–Bi (T = Cu, Au and Pt) systems. So far, we have succeeded in growing single crystals of $Ce_3Pt_3Bi_4$, $Ce_3Au_3Bi_4$, $CeAu_{1-x}Bi_2$ and $CeCu_{1-x}Bi_2$. Among these, the new ternary compound $CeCu_{1-x}Bi_2$ shows a sharp peak in magnetic susceptibility at about 12 K, indicating antiferromagnetic order. In addition, a stepwise magnetization as a function of magnetic field was observed below 12 K (Huang, Ye, Hirata & Kadowaki, 1995).

The X-ray diffraction analysis described in this work showed that $CeCu_{1-x}Bi_2$ is isotypic with $ZrCuSi_2$. The structure can be described as an intergrowth of Bi layers between CeBiCu slabs (Fig. 1). Bi atoms are located at the (100) and (010) face-centered positions of the tetragonal unit cell, and form sheets of Bi atoms in a square-lattice array. The CeBiCu slabs consist of $CeBiCu_4$ distorted octahedra with Ce and Bi atoms located at the two apices of the octahedra. These octahedra are connected to each other by sharing Cu—Cu edges, but the Ce and Bi atoms alternate on the apices. These two kinds of atomic layers stack alternately along the [001] direction *via* Ce—Bi and Bi—Bi bonds to form a three-dimensional network.

The large anisotropy in the displacement parameters for Bi2 and Cu, shown in Fig. 1, should be noted. It can be seen that Cu shows a larger displacement in the *xy* plane than in the *z* direction. In contrast,

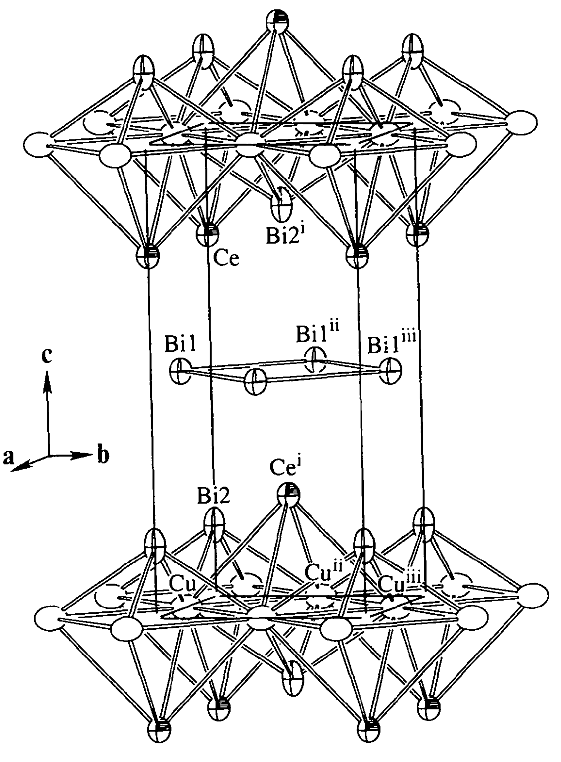

Fig. 1. *ORTEP*II (Johnson, 1976) illustration of $CeCu_{1-x}Bi_2$ (origin at 1/4, 1/4, 0 from center). Displacement ellipsoids are shown at the 90% probability level.

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