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BRIEF COMMUNICATIONS

The Crystal Structure of $Ca(ReO_4)_2 \cdot 2H_2O$

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The crystal structure of $Ca(ReO_4)_2 \cdot 2H_2O$ should be described in space group *C*2/*c*, not in space group *Cc* (R. G. Matveeva *et al.*, *Sov. Phys. Dokl.* **25,** 321, 1980), or in *C*2 (J. P. Picard *et al.*, *J. Solid State Chem.* **69,** 380, 1987). A crystal structure description based on an averaging of the two previous determinations agrees better with known interatomic distances and allows the assignment of a probable hydrogen bonding scheme. Space groups *Cc* and *C*2 are both monoclinic subgroups of order two of *C*2/*c*. Descriptions of crystal structures in polar space groups are often difficult to diagnose as being of unnecessarily low symmetry, because the overlooked symmetry elements are not in conspicuous places of the chosen unit cell. © 1992 Academic Press, Inc.

The crystal structure of $Ca(ReO_4)_2 \cdot 2H_2O$ was determined by Matveeva *et al.* (*1*) in the noncentrosymmetric monoclinic space group *Cc*, with the cell constants a = 18.895 Å, b = 7.078 Å, c = 14.212 Å, β = 115° 22′, and Z = 8. Actually these authors described the structure with the normal to the glide plane parallel to the *c*-direction, but we have transformed it here to the more commonly used setting with that normal parallel to the *b*-direction. This setting of (*1*) is used throughout this paper. Subsequently the crystal structure of $Ca(ReO_4)_2 \cdot 2H_2O$ was redetermined by Picard *et al.* (*3*), apparently independently of the previous work, in the likewise noncentrosymmetric monoclinic space group *C*2, with the cell constants a = 18.90 Å, b = 7.066 Å, c = 14.17 Å, β = 115.4°, and Z = 8. The cell constants in the two determinations are very similar to each other. The scatter in the individual bond lengths Re–O reported in these structures is unrealistically large. It ranges from 1.55 to 1.89 Å.

More than 10% of the crystal structures determined in space group *Cc* have been shown to be described in unnecessarily low symmetry (*4*). In some cases the true symmetry of these structures must be described in either the orthorhombic system (space group *Fdd*2) or in the rhombohedral system (space group $R\bar{3}c$). Very often, however, the true symmetry of these crystal structures is the corresponding monoclinic centrosymmetric space group *C*2/*c*, obtained from *Cc* by the addition of an inversion center or of a twofold rotor. This can often be diagnosed by the occurrence of bond lengths that deviate much from accepted values. These distortions are due to the strong correlations caused in the least-squares refinement of independently refined parame-

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TABLE I

DATA FOR $Ca(ReO_4)_2 \cdot 2H_2O$ (a = 18.8975 Å, b = 7.0720 Å, c = 14.1910 Å, β = 115.38°, Z = 8), SPACE GROUP *C*2/*c*, ALL ATOMS IN THE GENERAL POSITION 8*f* (*2*), POSITIONAL PARAMETERS IN FRACTIONAL COORDINATES

				M(*1*)		M(*1*)		P(*3*)		P(*3*)	
Atom	*x*	*y*	*z*	# *s*	*d*	# *s*	*d*	# *s*	*d*	# *s*	*d*
Re(1)	0.4242	0.3858	0.3162	1/8	0.060	2/7	0.059	2/2	0.004	4/6	0.003
Re(2)	0.8270	0.3379	0.4187	3/7	0.025	4/6	0.025	1/8	0.005	3/2	0.004
Ca(1)	0.3507	0.3510	0.5496	1/8	0.042	2/4	0.045	1/2	0.035	2/6	0.031
O(1)	0.521	0.464	0.373	1/7	0.16	2/8	0.20	12/2	0.10	13/5	0.15
O(2)	0.390	0.378	0.410	11/4	0.14	14/8	0.16	16/1	0.08	18/6	0.13
O(3)	0.370	0.452	0.723	12/4	0.14	15/3	0.07	8/1	0.14	9/6	0.19
O(4)	0.082	0.335	0.735	5/1	0.14	13/2	0.07	1/7	0.20	20/2	0.14
O(5)	0.201	0.444	0.562	3/8	0.16	6/2	0.13	7/1	0.20	10/6	0.16
O(6)	0.917	0.344	0.419	8/6	0.19	17/5	0.13	14/2	0.17	19/8	0.23
O(7)	0.762	0.264	0.297	9/6	0.18	16/7	0.14	3/8	0.14	4/2	0.06
O(8)	0.672	0.317	0.485	10/4	0.12	18/6	0.11	2/8	0.08	5/2	0.07
Ow(1)	0.219	0.379	0.382	4/8	0.09	20/5	0.12	6/1	0.09	11/6	0.11
Ow(2)	0.051	0.381	0.371	7/6	0.16	19/5	0.14	15/1	0.18	17/6	0.23

Symmetry transformations, *s*

1:	x	y	z	2:	$-x$	y	$-z + \frac{1}{2}$
3:	$x + \frac{1}{2}$	$y + \frac{1}{2}$	z	4:	$-x + \frac{1}{2}$	$y + \frac{1}{2}$	$-z + \frac{1}{2}$
5:	$-x$	$-y$	$-z$	6:	x	$-y$	$z + \frac{1}{2}$
7:	$-x + \frac{1}{2}$	$-y + \frac{1}{2}$	$-z$	8:	$x + \frac{1}{2}$	$-y + \frac{1}{2}$	$z + \frac{1}{2}$

Note. The identification of the atoms in the previous crystal structure determinations is given in columns M (*1*) and P (*3*). The sequence in each column is #/*s* *d*, where # is the original numbering of the atoms in either Ref. (*1*) or (*3*); *s* is the symmetry operation in space group *C*2/*c*, see bottom of this table, which transforms the coordinates in this table to the coordinates in the original papers, after transformation and shift in origin as given in the text; *d* is the distance (Å) from the coordinates given here to those of the original papers when correctly transformed.

ters in the subgroup that would actually be related by a center of symmetry in the true higher symmetric space group (*5*). This latter instance seems to be the case in the two structure determinations of $Ca(ReO_4)_2 \cdot 2H_2O$. It appears that the true space group of this compound should be *C*2/*c*, and that it has been described once in *Cc*, one of the monoclinic maximal subgroups of order two of *C*2/*c*, and the other time in the second monoclinic maximal subgroup of order two *C*2/*c*, namely *C*2. In order to verify this assumption we checked both crystal structures using the computer program MISSYM (*6*). In both cases a glide plane normal to the *b* cell direction was identified, thus the most likely space group appears to be *C*2/*c*.

When the coordinates of the atoms of $Ca(ReO_4)_2 \cdot 2H_2O$ described in space group *Cc* (*1*) are shifted to $x_{new} = x_{old} + 0.332$ and $z_{new} = z_{old} + 0.411$ an inversion center is located at the origin. All atomic positions are pairwise related by that center and on average removed only 0.11 Å from their mean positions. The smallest deviations are observed for the Re (0.060 and 0.025 Å) and Ca atoms (0.043 Å), the largest for a pair of oxygen atoms (0.18 Å). A description in space group *C*2/*c* is thus warranted by a comparison of the coordinates of related

TABLE II

INTERATOMIC DISTANCES (Å) IN $Ca(ReO_4)_2 \cdot 2H_2O$

Environments of the cations							
Re(1)–O(4)	1.71	Re(2)–O(5)	1.69	Ca–Ow(2)	2.37	Ca–Ow(1)	2.53
Re(1)–O(2)	1.72	Re(2)–O(6)	1.71	Ca–O(2)	2.39	Ca–O(1)	2.55
Re(1)–O(3)	1.72	Re(2)–O(7)	1.72	Ca–O(8)	2.40	Ca–O(5)	2.56
Re(1)–O(1)	1.74	Re(2)–O(8)	1.75	Ca–O(3)	2.43	Ca–Ow(1)	2.62
Re(1)–O_{mean}	1.72	Re(2)–O_{mean}	1.72		Ca–O_{mean} 2.48		
Possible hydrogen bonds							
Ow(1)–O(7)	2.83	Ow(1)–O(4)	3.24	Ow(2)–O(6)	2.89	Ow(2)–O(4)	3.01

pairs of atoms. Incidentally the comparison reveals that the *y*-coordinate of atom O(15) is misprinted in the original paper (*1*), it should read −0.0537 instead of 0.0537.

An analogous shift of the positional coordinates in the structure described in space group *C*2 (*3*) by $y_{new} = y_{old} - 0.162$ and $z_{new} = z_{old} + 0.250$ brings likewise a corresponding center of symmetry into the origin. In this case the mean distance from each atom of a related pair to its mean is again 0.11 Å, the largest deviation is observed for two oxygen atoms (0.20 Å), and the positions of the Re atoms fit even better (0.005 and 0.003 Å) to each other. Again space group *C*2/*c* seems likely for the proper description of the crystal structure.

When the two original structure determinations of $Ca(ReO_4)_2 \cdot 2H_2O$ described in space group *C*2/*c* are compared with each other, the agreement between them is excellent. The average distance of each pair of atoms from their mean is only 0.022 Å, the Re atoms deviate by 0.001 Å from their mean, the worst fit is again observed for a pair of oxygen atoms (0.040 Å). There can be no reasonable doubt that the two structures are identical. The averaged coordinates for the two structure determinations, cast in the description in space group *C*2/*c* are given in Table I, the resulting bond lengths in Table II.

The main features of the crystal structure of $Ca(ReO_4)_2 \cdot 2H_2O$ as described in the previous papers (*1*, *3*) are still valid. However, the details conform now much better with crystal chemical experience. The maximum spread in Re–O bond lengths after the coordinates of the atoms of the two crystal structures have been averaged in the manner described above is only 0.06 Å (Table II), as compared to 0.34 Å before. The mean distance Re–O observed now (1.72 Å) is very close to the distance of 1.73 Å obtained from the sum of the effective ionic radii of Re^{7+} and O^{2-} (*7*). From the remaining variation in the Re–O bond lengths we judge the estimated standard deviations of the oxygen positions to be in the vicinity of about 0.02 Å (or about 0.001 in terms of the fractional coordinates of Table I).

The improved precision of the crystal structure determination based on an averaging of the original coordinates allows also a probable assignment of hydrogen bonds based on the usual criteria (*8*). Oxygen atoms O(4), O(6), and O(7) are not coordinated to the calcium atom. Therefore, they are likely hydrogen bond acceptors. Oxygen atom Ow(2) is bonded once to the calcium atom and has oxygen atoms O(4) and O(7) within hydrogen bonding range (Table II). The angles Ca–Ow(2)–O(6), Ca–Ow(2)–O(4), and O(4)–Ow(2)–O(6) add up to 360°, thus this arrangement is strictly planar. The oxygen atom of water molecule Ow(1) is bonded twice to the calcium atom, and has two distances to O(4) and O(6) within approximate hydrogen bonding range (Table II). The distance to O(4) is slightly too long, but we have to bear in mind that atom O(4) already is an acceptor of a hydrogen bond from Ow(2). Oxygen atoms O(4) and O(7) and the two calcium neighbors surround Ow(2) in an approximately tetrahedral fashion.

The reason why in the original descriptions of this crystal structure the higher symmetry was overlooked is most likely that in polar space groups it is often difficult to diagnose the higher symmetry because the overlooked symmetry elements are not in conspicuous places of the chosen unit cell (*4*). However, the two crystal structure determinations have, when taken together, described the true symmetry ($C2 + Cc = C2/c$) and after proper averaging also the geometry of the bonds in $Ca(ReO_4)_2 \cdot 2H_2O$ quite correctly.

Computer programs used in this work were MISSYM (*6*), SADIAN90 (*9*), and a set of programs (SYMM) written by Kassner for the manipulation of symmetry information.

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