

CoReO₄, a New Rutile-Type Derivative with Ordering of Two Cations

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CoReO₄ crystallizes in space group *Cmmm* with $a = 6.5156(7) \text{ \AA}$, $b = 6.7418(8) \text{ \AA}$, $c = 2.8923(3) \text{ \AA}$. It is most likely to be formulated as Co⁺³Re⁺⁵O₄. The bonding topology of the connections of the coordination octahedra around the Co and the Re atoms is identical to the arrangement of the coordination octahedra in the rutile type. Octahedral edge-sharing rutile-type chains of compositions CoO₄ and ReO₄ are present which are connected via corners, resulting in an overall chemical formula of CoReO₄. The space group type of CoReO₄, *Cmmm*, is a maximal nonisomorphic subgroup of order two of the space group type of rutile, *P4₂/mnm*; it is translationengleich with its supergroup. The space group type of MgUO₄, *Imam*, is in turn a maximal nonisomorphic subgroup of order two of space group *Cmmm*; it is klassengleich with its supergroup. Thus the structure type of CoReO₄ can be seen as an intermediate step in the reduction of the symmetry of the rutile type proper to the distorted rutile-type variant represented by MgUO₄. The crystal structure of CoReO₄ represents a new type derived from the rutile type by ordering of two cations. It is the fourth structure type of this kind. © 1992 Academic Press, Inc.

Introduction

Sleight reported (1) the synthesis of several rhenium compounds apparently related to the rutile type: AlReO₄, GaReO₄, FeReO₄, NiReO₄, and CoReO₄. The first three yielded tetragonal cell constants in a small unit cell analogous to rutile itself (approximately 4.7 by 4.7 by 2.9 Å), and thus most likely belong to the rutile type and have a statistical occupancy of the metal atom position by Re and either Al, Ga, or Fe. The remaining two compounds were described as clearly orthorhombic. The cobalt compound was in addition found to crystallize in a C-centered cell with $a = 6.503 \text{ \AA}$, $b = 6.732 \text{ \AA}$, $c = 2.881 \text{ \AA}$, that is with a and

b cell constants larger by a factor of 2^{1/2} compared to the rutile type itself or to NiReO₄ (1). We thought, therefore, that CoReO₄ had an ordered distribution of Co and Re atoms within its crystal structure. Furthermore we suspected that it was not similar to any of the other three known variants of the rutile-type structure with an ordering of two cations. These are: 1. MgUO₄, $a = 6.520 \text{ \AA}$, $b = 6.595 \text{ \AA}$, $c = 6.924 \text{ \AA}$, space group *Imam* (2), where the rutile-type chains of edge-sharing octahedra have the compositions MgO₄ and UO₄, are arranged parallel to [001] and share vertices the same way as the octahedral chains in rutile do; 2. CuUO₄, $a = 5.475 \text{ \AA}$, $b = 4.957 \text{ \AA}$, $c = 6.569 \text{ \AA}$, $\beta = 118.87^\circ$, space group *P2₁/n* (3), where

the Cu and U atoms alternate within the chains of edge-sharing octahedra; 3. AlWO_4 , $a = 9.069 \text{ \AA}$, $b = 5.705 \text{ \AA}$, $c = 4.541 \text{ \AA}$, $\beta = 92.29^\circ$, space group $C2/m$ (4), where the Al and W atoms are distributed over separate octahedral chains as in MgUO_4 , and in addition pairs of tungsten atoms approach each other over the shared edge, apparently forming weak bonds to each other (distance W–W 2.61 Å). Obviously the description of the unit cell and symmetry of CoReO_4 does not fit any of these three variants of the rutile type.

Experimental

For the sample preparation see Ref. (1). A crystal of approximate dimensions of $0.13 \times 0.15 \times 0.25 \text{ mm}$ was selected for single crystal work. Laue photographs had shown that it was of poor quality (large mosaic spread), but other selected crystals were even worse. Diffraction data were measured over almost a complete sphere of reflection on an Enraf-Nonius CAD4 diffractometer with $\text{MoK}\alpha$ radiation (wavelength = 0.7107 \AA). Within a range of $2\theta = 60^\circ$, a total of 692 reflections were measured. Crystal orientation and stability of the radiation intensity were monitored by measuring repeatedly three standard reflections. Absorption was corrected empirically by the psi-scan procedure. After averaging 126 unique reflections were obtained with an internal R -value of 4.55%. The observed systematic extinctions indicated space group $Cmmm$. Because of the poor quality of the single crystal the resulting cell constants were considered to be unreliable. A powder pattern was taken of the sample on a Siemens D500 diffractometer and a Rietveld-type refinement yielded the cell constants $a = 6.5156(7) \text{ \AA}$, $b = 6.7418(8) \text{ \AA}$, and $c = 2.8923(3) \text{ \AA}$, in reasonable agreement with the values reported in Ref. (1). A model in space group $Cmmm$ was derived from the parent rutile type structure (space group

$P4_2/mnm$) and checked for possible orientations of the orthorhombic cell axes as compared to the tetragonal axes and for different distributions of the Co and Re atoms over the special positions. The model with the best agreement between F_{obs} and F_{calc} was used for the refinement of the single crystal diffraction data with isotropic temperature factors for the Co, O(1), and O(2) atoms and anisotropic temperature factors for the Re atom. It yielded an R -value of 5% and the structural parameters given in Table I and the bond lengths and angles given in Table II.

Results and Discussion

The bonding topology of the connections of the coordination octahedra around the Co and the Re atoms in this compound is identical to the arrangement of the coordination octahedra in the rutile type. Octahedral edge-sharing rutile-type chains of compositions CoO_4 and ReO_4 are present which are connected via corners resulting in an overall chemical formula of CoReO_4 (see Figs. 1 and 2). In this respect CoReO_4 is similar to MgUO_4 (2), however, the ordering of the two types of cation over two separate chains is accomplished here in a cell with half the volume of the unit cell of MgUO_4 . In fact the volume of the primitive unit cell of CoReO_4 is in principle the same as in rutile itself (TiO_2). Apparently the tendency of the uranium atom to form dumbbell-shaped linear uranyl groups O–U–O with very short uranium–oxygen bonds causes a distortion of the octahedral framework which can be accommodated only in the larger cell of MgUO_4 .

The space group type of CoReO_4 , $Cmmm$, is a maximal nonisomorphic subgroup of order two of the space group type of rutile (TiO_2), $P4_2/mnm$ (5). In this lowering of symmetry the volume of the primitive unit cell remains the same (it is translationgleich, see Ref. (6)), but some of the sym-

TABLE I
DATA FOR CoReO_4 ($a = 6.5156(7)$ Å, $b = 6.7418(8)$ Å, $c = 2.8923(3)$ Å), SPACE GROUP $Cmmm$

Atom	x	y	z	U	Wyckoff position	Site symmetry
Co	0	0	0	0.0011(9)	2(<i>a</i>)	<i>mmm</i>
Re	$\frac{1}{2}$	0	$\frac{1}{2}$	0.0123(8) ^a	2(<i>c</i>)	<i>mmm</i>
O(1)	0	0.296(4)	0	0.021(5)	4(<i>i</i>)	<i>m2m</i>
O(2)	0.217(3)	0	$\frac{1}{2}$	0.017(5)	4(<i>h</i>)	<i>2mm</i>

^a $U_{11} = 0.0080(6)$; $U_{22} = 0.0038(8)$; $U_{33} = 0.0251(11)$.

Note. Positional parameters in fractional coordinates; temperature factors (Å^2); U is $U_{\text{isotropic}}$ for Co, O(1), and O(2) and $U_{\text{equivalent}}$ for Re; Wyckoff positions; site symmetry, see Ref. (5).

metry elements of space group $P4_2/mnm$ are removed. The space group type of MgUO_4 , $Imam$, is in turn a maximal nonisomorphic subgroup of order two of space group $Cmmm$. This is accompanied by a doubling of the effective cell volume achieved by a doubling of the c cell constant, but the resulting symmetry remains in the same crystallographic point group as before (it is klassesgleich, see Ref. (6)). Thus the structure type of CoReO_4 can be seen as an intermediate step in the reduction of the symmetry of the rutile type proper to the distorted rutile-

type variant represented by MgUO_4 (Fig. 3). It fills in one of the gaps remaining in the Bärnighausen-tree (6) of the rutile-type family presented by Meyer (7).

The reduction of symmetry from the rutile type, space group type $P4_2/mnm$ to the CaCl_2 type, space group type $Pnmm$, is also of order two, and also leads to orthorhombic symmetry. However, in the CoReO_4 type the diagonal mirror planes of the tetragonal space group are preserved, while in $Pnmm$ they are lost. Thus in the CaCl_2 type the anions are free to assume an arrangement

TABLE II
INTERATOMIC DISTANCES (Å) AND ANGLES
(°) IN CoReO_4

Environments of the cations			
2 × Co–O(1)	2.00(3)	4 × Re–O(1)	2.00(2)
4 × Co–O(2)	2.02(2)	2 × Re–O(2)	1.84(2)
Co–O _{mean}	2.01	Re–O _{mean}	1.95
2 × Co–Co	2.8923(3)	2 × Re–Re	2.8923(3)
4 × Co–Re	3.5644(5)	4 × Re–Co	3.5644(5)
4 × Co–Re	3.6680(5)	4 × Re–Co	3.6680(5)
8 × O(1)–Co–O(2)	90	8 × O(1)–Re–O(2)	90
1 × O(1)–Co–O(1)	180	2 × O(1)–Re–O(1)	180
2 × O(2)–Co–O(2)	180	1 × O(2)–Re–O(2)	180
2 × O(2)–Co–O(2)	88.7(6)	2 × O(1)–Re–O(1)	87.1(8)
2 × O(2)–Co–O(2)	91.3(6)	2 × O(1)–Re–O(1)	92.9(8)
Environments of the oxygen atoms			
4 × O(1)–O(2)	2.72(2)	4 × O(2)–O(1)	2.72(2)
1 × O(1)–O(1)	2.75(4)	1 × O(2)–O(2)	2.83(3)
4 × O(1)–O(2)	2.84(2)	4 × O(2)–O(1)	2.84(2)
2 × O(1)–O(1)	2.8923(3)	2 × O(2)–O(2)	2.8923(3)
2 × Co–O(1)–Re	133.6(6)	2 × Co–O(2)–Re	134.4(4)
1 × Re–O(1)–Re	92.9(11)	1 × Co–O(2)–Co	91.3(8)

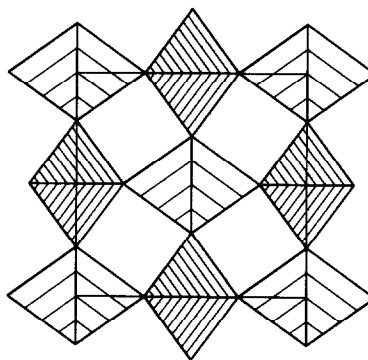


FIG. 1. CoReO_4 , view parallel [001]. The more densely shaded octahedra correspond to the ReO_6 octahedra, the lighter shaded to the CoO_6 octahedra. Origin is in lower left, a extends from bottom to top, b from left to right. The unit cell outline is indicated. The rutile-type chains are viewed from the top; they extend into the drawing. The drawing was made with the help of STRUPL090 (14).

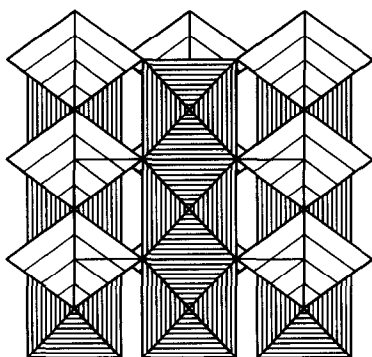


FIG. 2. CoReO_4 , view parallel $[100]$. Origin is in lower left, b extends left to right, c from bottom to top; for an explanation of the shading and all other details see the legend to Fig. 1. The rutile-type chains extend from bottom to top.

close to hexagonal closest packing, while in CoReO_4 the oxygen atoms remain on the diagonal mirror planes, which here are normal to $[100]$ and $[010]$. Therefore, the oxygen atoms in CoReO_4 are 11-coordinated around each other in tetragonal close packing as shown by Baur (8) for the rutile type proper (Table II).

The mean distance $\text{Re}-\text{O}$ of 1.95 \AA (Table II) agrees best with the assumption that rhenium has a formal charge of $+5$. Using

Shannon's radii (9) the bond length $\text{Re}^{+5}-\text{O}$ should measure 1.94 \AA , while $\text{Re}^{+6}-\text{O}$ should be 1.91 \AA . If this is the case, then cobalt should be present as Co^{+3} , in high spin state, and the observed $\text{Co}-\text{O}$ distance of 2.01 \AA would then be reasonably close to the sum of the radii for $\text{Co}^{+3}-\text{O}$ of 1.97 \AA . In this comparison one has to bear in mind that the precision of the crystal structure determination is not very high. The rather large difference in the bond lengths $\text{Re}-\text{O}(1)$ and $\text{Re}-\text{O}(2)$, see Table II, can be interpreted as due to over- and underbonding of the two oxygen atoms (10). This argument is also useful for preferring an interpretation of this compound as $\text{Co}^{+3}\text{Re}^{+5}\text{O}_4$. The sum of the bond strengths at $\text{O}(1)$ is 2.17 valence units and 1.83 valence units at $\text{O}(2)$ for a $+3/+5$ compound. If the compound were to be formulated as $\text{Co}^{+2}\text{Re}^{+6}\text{O}_4$ the sums of the bond strengths would be 2.33 and 1.67 valence units (see Ref. (10)). The amount of over- and underbonding at the two oxygen atoms is much reduced in $\text{Co}^{+3}\text{Re}^{+5}\text{O}_4$. In this context it is of interest that VSbO_4 , which because of its cell constants and of its C-centering should be isostructural with CoReO_4 , is being interpreted on the basis of Mössbauer spectra as $\text{V}^{+3}\text{Sb}^{+5}\text{O}_4$ (11).

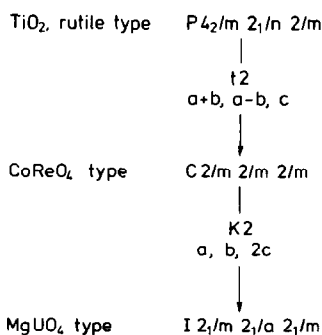


FIG. 3. Symmetry reduction from the rutile type structure, over the CoReO_4 -type structure to the MgUO_4 -type structure. The unit cell relations, the type (t for translationgleich, k for klassengleich), and the order of the symmetry reduction are indicated.

Acknowledgments

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References

1. A. W. SLEIGHT, *Inorg. Chem.* **14**, 597 (1974).
2. W. H. ZACHARIASEN, *Acta Crystallogr.* **7**, 788 (1954).
3. S. SIEGEL AND H. R. HOEKSTRA, *Acta Crystallogr., Sect. B*, **24**, 967 (1968).
4. J. P. DOUMERC, M. VLASSE, M. POUCHARD, AND

- P. HAGENMÜLLER, *J. Solid State Chem.* **14**, 144 (1975).
5. T. HAHN, Ed., "International Tables for Crystallography," Reidel, Dordrecht (1983).
 6. H. BÄRNIGHAUSEN, *MATCH* **9**, 139 (1981).
 7. A. MEYER, Thesis Karlsruhe (1981).
 8. W. H. BAUR, *Mater. Res. Bull.* **16**, 339 (1981).
 9. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
 10. W. H. BAUR, *Trans. Am. Crystallogr. Assoc.* **6**, 129 (1970).
 11. T. BIRCHALL AND A. W. SLEIGHT, *Inorg. Chem.* **15**, 868 (1976).
 12. G. M. SHELDRICK, "SHELX76," University of Cambridge, England (1976).
 13. C. J. HOWARD AND R. J. HILL, AAEC Report No. M112 (1986).
 14. R. X. FISCHER, A. LE LIRZIN, D. KASSNER, AND B. RÜDINGER, *Z. Kristallogr. Suppl. Issue* **3**, 75 (1991).
 15. W. H. BAUR AND D. KASSNER, *Z. Kristallogr. Suppl. Issue* **3**, 15 (1991).