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Structure of Rhenium Disulfide

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Introduction

Transition metal sulfides are widely used commercially in hydrotreating processes[1] and found as minerals in nature.[2,3] Rhenium disulfide and rhenium diselenide have been studied by numerous workers in a variety of disciplines.[4−12] In describing the structure of ReS_2, many investigators[5,9,10,12−14] reference the work on the dichalcogenides of technetium and rhenium by Wildervanck and Jellinek[15] and assume that ReS_2 is isostructural[16] with the published structure of $ReSe_2$.[17,18] The single-crystal X-ray diffraction study presented here indicates ReS_2 is not isostructural with the reported $ReSe_2$ structure. The single-crystal X-ray diffraction study of rhenium disulfide is critical in studying the atomic-scale structural and electronic properties of transition metal sulfides[19] and in the development of soluble, discrete molecules which contain metal−sulfur cores that are structurally similar to portions of the rhenium disulfide lattice.[13]

Table 1. Crystallographic Data for ReS_2

chem formula	ReS_2	fw	250.32
a, Å	6.417(4)	space group	$P\bar{1}$ (No. 2)
b, Å	6.510(4)	T, °C	20 ± 1
c, Å	6.461(4)	λ, Å	0.710 73
α, deg	121.10(4)	ϱ_{calcd}, g·cm^{-3}	7.581
β, deg	88.38(5)	μ, mm^{-1}	56.84
γ, deg	106.47(5)	R_1[a]	0.067
V, Å^3	219.3(2)	R_2[b]	0.092
Z	4		

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 × 10) for ReS_2[a]

atom	10^4x	10^4y	10^4z	B, Å^2 × 10
Re_1	4925(1)	564(1)	2477(1)	2(1)
Re_2	5026(1)	5112(1)	2974(1)	2(1)
S_1	2174(10)	2498(10)	3676(9)	6(1)
S_2	2769(9)	7705(9)	3819(8)	3(1)
S_3	7562(9)	2729(9)	1178(8)	3(1)
S_4	6975(9)	7526(9)	1169(9)	4(1)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

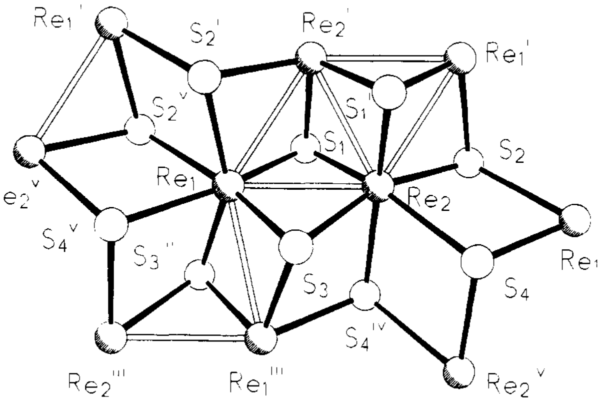

Figure 1. Perspective drawing of the contents and coordination spheres for the asymmetric unit of ReS_2 viewed down the $\overline{a}$ axis. Re···Re distances less than 2.90 Å are represented by open bonds.

Experimental Section

ReS_2. Crystals of ReS_2 were grown by chemical vapor transport as described by Wold and co-workers.[20] Crystallographic data and details of the parameters associated with data collection and structure refinement are given in Table 1 and the supplementary material. A total of 1288 independent absorption-corrected reflections having 2Θ(Mo Kα) < 60.4° were collected on a computer-controlled Nicolet autodiffractometer using full (3.80°-wide) ω scans and graphite-monochromated Mo Kα radiation. The structure was solved using direct methods techniques with the Siemens SHELXTL-PC software package as modified at Crystalytics Co. The resulting structural parameters have been refined to convergence [R_1(unweighted, based on F) = 0.067 for 1098 independent absorption-corrected reflections having 2Θ(Mo Kα) < 60.4° and $I > 3\sigma(I)$] using counter-weighted full-matrix least-squares techniques and a structural model which incorporated isotropic thermal parameters for all Re and S atoms.[21] Fractional coordinates and isotropic thermal parameters are given in Table 2.

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(16) As used here, "isostructural" is a general term referring to the similarity of fractional coordinates of corresponding atoms in different structures.

(17) Alcock, N. W.; Kjekshus, A. *Acta Chem. Scand.* **1965**, *19*, 79−94.

(18) In order to determine whether or not the structure reported herein for ReS_2 is isostructural with the published structure of $ReSe_2$ the F_o data for $ReSe_2$ published by Alcock were used in two different unit-weighted full-matrix least-squares $ReSe_2$ refinements with Se scattering factors, the first using the ReS_2 coordinates from this work and the second starting with the published $ReSe_2$ coordinates. These refinements used published lattice constants for $ReSe_2$ and gave R_1 values of 0.079 and 0.088, respectively, for 6 isotropic atoms and 26 variables. This suggests that an alternate structure may be possible.

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(21) There are two ways of choosing axes for the triclinic unit cell of ReS_2: (1) a_1 = 6.417 Å, b_1 = 6.377 Å, c_1 = 6.461 Å, α_1 = 119.06°, β_1 = 91.62°, and γ_1 = 105.12°; (2) a_2 = 6.417 Å, b_2 = 6.510 Å, c_2 = 6.461 Å, α_2 = 121.10°, β_2 = 88.38°, and γ_2 = 106.47° where $a_2 = -a_1$, $b_2 = -b_1 - c_1$, and $c_2 = c_1$. The first was used to collect the

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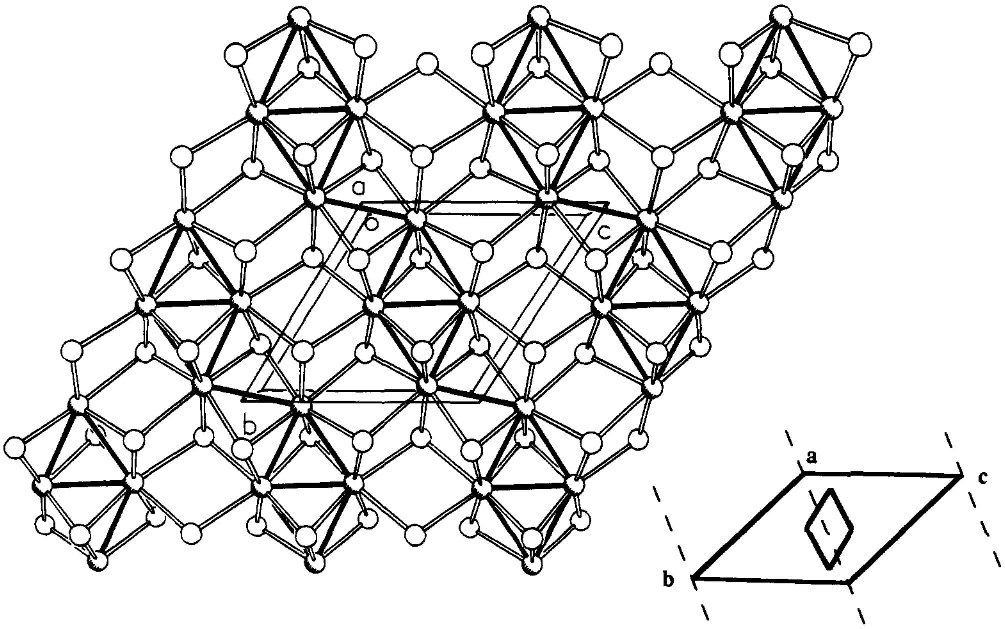

Figure 2. Perspective drawing down the $\vec{a}$ axis showing the chains of Re_4 parallelograms (Re• • •Re <2.90 Å: solid lines). Re atoms are represented as shaded circles, sulfur atoms as open circles, and Re—S bonds as open bonds.

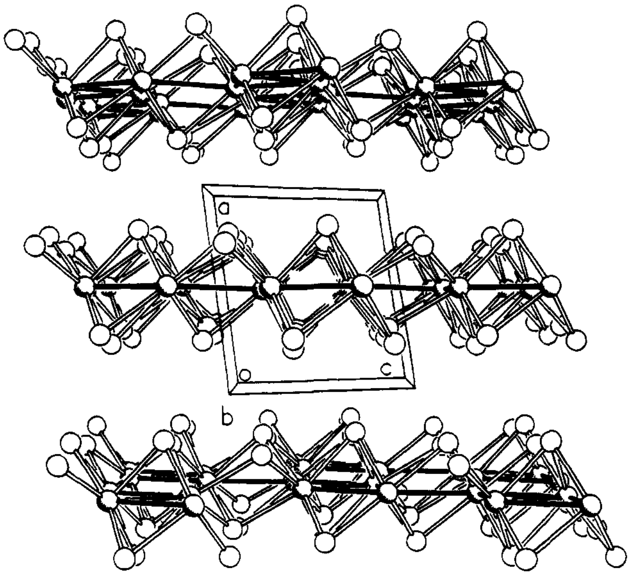

Figure 3. Perspective drawing down the $\vec{b}$ axis showing the rippling effect of the sulfur atom layer. Re atoms are represented as shaded circles, sulfur atoms as open circles, Re• • •Re <2.90 Å as solid lines, and Re—S bonds as open bonds.

Results and Discussion

The asymmetric unit of rhenium disulfide consists, formally, of two Re^{4+} and four S^{2-} ions (Re_1, Re_2, S_1, S_2, S_3, S_4) (Figure 1) and is similar to the solid-state structure of $CdCl_2$. Layers of nearly hexagonal-close-packed arrays (Figure 2) of sulfur atoms stack (Figure 3) along the *a* axis and are nearly parallel to the *bc* plane of the unit cell. The Re atoms occupy the octahedral sites between every other pair of these hexagonal-close-packed layers of sulfur atoms. Each rhenium is coordinated to six sulfur atoms in approximately octahedral geometry, and each trigonal pyramidal sulfur atom is bonded to three Re atoms. The participation of each d^3-Re atom in the formation of metal—metal bonds to three neighbors in the layer of cations results in the formation of Re_4 parallelograms (Figure 1) with their acute vertices linked together in a linear fashion (Figure 2) by 2.895(2) Å Re—Re bonds. Each Re_4 parallelogram is formed by two triangles of metal—metal-bonded Re atoms sharing an edge; the Re—Re edges of the parallelogram are 2.790(1) and 2.824(1) Å, and the shared edge is 2.695(1) Å. This is the shortest of the Re—Re bonds and is a result of being constrained by the four bonds of the parallelogram. The distance between rhenium atoms in the metal[22] are 2.740 and 2.761 Å. The metal—metal-bonding network of ReS_2 has been discussed by Burdett[23] and Whangbo.[24] Nonbonded Re—Re separations between adjacent metals in the cation layer range from 3.560(1) to 3.770(2) Å. See Table 3 for bond lengths of ReS_2.

Table 3. Bond Lengths (Å) in Crystalline ReS_2[a,b]

	Re—Re Bonds		
Re_2—Re_2^{i}	2.695(2)	Re_1• • •Re_2^{iii}	3.560(1)
Re_1—Re_2	2.790(2)	Re_1• • •Re_1^{ii}	3.703(2)
Re_1—Re_2^{i}	2.824(2)	Re_1• • •Re_2^{v}	3.744(1)
Re_1—Re_1^{iii}	2.895(2)	Re_2• • •Re_2^{iv}	3.770(2)
	Re—S Bonds		
Re_1—S_1	2.341(7)	Re_2—S_1	2.331(6)
Re_1—S_2^{v}	2.504(7)	Re_2—S_1^{i}	2.344(5)
Re_1—S_2^{i}	2.379(6)	Re_2—S_2	2.374(7)
Re_1—S_3	2.311(6)	Re_2—S_3	2.422(6)
Re_1—S_3^{iii}	2.400(4)	Re_2—S_4	2.468(7)
Re_1—S_4^{v}	2.458(7)	Re_2—S_4^{iv}	2.441(5)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Table 2. Atoms labeled with a superscripted i—v are related to atoms without these subscripts by the following symmetry operations: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, -y, -z$; (iv) $1 - x, 1 - y, -z$; (v) $x, -1 + y, z$; (vi) $x, 1 + y, z$.

The Re—Re bonds forming the parallelogram have a significant effect on the relative displacements of the sulfur atoms within their hexagonal-close-packed arrays. These parallelograms are within 1.3° of being coplanar with the *bc* plane

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ReS_2 diffraction data, identify faces for the absorption correction, and solve the structure; the ReS_2 data and coordinates were transformed to the second description when it was realized that the published structure for $ReSe_2$ probably used the second choice of axes.

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of the unit cell and can be used to define a "basal" plane from which sulfur atom displacement can be measured. The displacement of coordinated sulfur atoms from this "basal" plane into the space between $[ReS_2]_x$ layers is seen to be closely correlated with the number of metal—metal bonds between the three metals it spans. Thus, S_1, which spans three metal—metal-bonded Re atoms, is displaced by 1.71 Å, S_3, which spans two metal—metal-bonded Re atoms, is displaced by 1.58 Å, S_2, which spans a single metal—metal bond, is displaced by 1.41 Å, and S_4, which spans no metal—metal bonds, is displaced by 1.14 Å. As can be seen in Figure 3, these displacements give a rippled appearance to the layer of S atoms.

Conclusion. ReS_2 is not "isostructural" with the published $ReSe_2$ structure as previously reported. A thorough re-examination of the structure of $ReSe_2$ may be warranted.

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Supplementary Material Available: Tables of crystallographic data and details of the parameters associated with data collection and structure refinement, complete bond angles, nonbonding distances, and torsion angles for ReS_2 (11 pages). Ordering information is given on any current masthead page.