

The crystal structure of pararealgar, As₄S₄

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ABSTRACT

Pararealgar, a polymorph of realgar (α -As₄S₄), crystallizes in the monoclinic space group $P2_1/c$, with $a = 9.909(2)$, $b = 9.655(1)$, $c = 8.502(1)$ Å, $\beta = 97.29(1)^\circ$, $V = 806.8(2)$ Å³. A single crystal of pararealgar was obtained by light exposure of realgar. The structure was determined by direct methods and refined by least-squares technique to a final R index of 3.39%. The structure consists of discrete covalently bonded As₄S₄ molecules, which are held together by van der Waals forces. In each molecule, one As atom links 2As + 1S, another links 3S, and the other two link 1As + 2S. Therefore this molecule differs from that of α -As₄S₄ but is the same as that found in As₄S₄(II). The difference between the structure of pararealgar and As₄S₄(II) is due to different molecular packing.

INTRODUCTION

Many studies have been made concerning the crystal structures, phase transitions, and stability fields of the As₄S₄ polymorphs. A number of phases are known: realgar (α -As₄S₄) (Ito et al., 1952; Pen'kov and Safin, 1963; Hall, 1966; Forneris, 1969; Mullen and Nowacki, 1972; Bues et al., 1983; Bryndzia and Kleppa, 1988), pararealgar (Roberts et al., 1980); and the χ phase referred to by Douglass et al. (1992) as the precursor to pararealgar formation. Two other phases, reported as high-temperature forms, are also described: β -As₄S₄ (Hall, 1966; Clark, 1970; Street and Munir, 1970; Porter and Sheldrick, 1972; Roland, 1972; Yu and Zoltai, 1972) and As₄S₄(II), synthesized and studied by Kutoglu (1976). Furthermore, Hall (1966) observed a thin orange-yellow film coating most museum specimens of realgar, called γ -AsS, which he was able to produce by exposing both natural and synthetic realgar to infrared radiation.

Pararealgar from two localities in British Columbia (Mount Washington on Vancouver Island and the Gray Rock property, Lillooet district), was first identified by Roberts et al. (1980), who described it as a new polymorph of AsS. According to these authors, the symmetry of pararealgar is monoclinic, with space group Pc or $P2_1/c$, and cell parameters $a = 9.929(4)$, $b = 9.691(6)$, $c = 8.503(3)$ Å, and $\beta = 97.06(2)^\circ$. Pararealgar always occurs as an alteration product of realgar. Since it resembles orpiment, pararealgar remained unidentified for a long time (Roberts et al., 1980). Recently Douglass et al. (1992) confirmed that the well-known friable degradation product of realgar that has been exposed to light consists of pararealgar. They emphasized that it is the stable AsS polymorph in the presence of light, whereas the formation of As₂S₃ requires a much higher pressure of S than what is normally present in air.

Until now, the crystal structure of pararealgar was unknown, and only a few hypotheses had been put forward.

On the basis of its cell parameters and X-ray powder pattern, pararealgar was supposed to be related to β -As₄S₄ (Roberts et al., 1980). Douglass et al. (1992) suggested that the lack of alteration in samples of realgar from Mina Alacrán, Chile (Clark, 1970), that had been exposed to sunlight for a long time could be related to coexisting β -As₄S₄. The same authors hypothesized that the structural similarity of β -As₄S₄ to pararealgar may preclude its formation where the β form occurs.

EXPERIMENTAL AND STRUCTURE SOLUTION

A suitable single crystal of pararealgar was obtained from an unaltered fragment of realgar from Hunan, China, through exposure to unfiltered visible light for 48 h. The light source was a 15-V and 150-W quartz-tungsten-halogen lamp manufactured by Philips; optical fibers were employed to minimize overheating. After the treatment, the crystal changed color from red to yellow and cracked into a number of minute fragments. One of these, because of its transparency, was chosen for the structural study.

Lattice parameters were determined by means of the least-squares method using 25 high- θ reflections measured with a CAD4 single-crystal diffractometer. Their values (Table 1) compare favorably with those measured by Roberts et al. (1980) and are in better agreement with the reported density. The systematic absences of $0k0$ ($k = 2n + 1$) and $h0l$ reflections ($l = 2n + 1$) led to the unique choice of space group $P2_1/c$. Intensity data were collected and subsequently corrected for Lorentz and polarization factors and for absorption (North et al., 1968). The crystal structure was solved using MULTAN-80 (Main et al., 1980). All the As and S atoms were located on the F_o -Fourier map, and isotropic full-matrix least-squares refinement led to $R = 7.0\%$. With the introduction of anisotropic displacement parameters and $w = 1/\sigma_{F_o}^2$, the structure refinement converged to a final R_w of 3.39%. The atomic scattering factors for neutral atoms

TABLE 1. Crystal data and experimental details for pararealgar

Crystal system	monoclinic
Space group	$P2_1/c$
Cell parameters	
a (Å)	9.909(2)
b (Å)	9.655(1)
c (Å)	8.502(1)
β (°)	97.29(1)
V (Å ³)	806.8(2)
Formula units per unit cell, Z	4
Diffractometer	Enraf Nonius CAD4
Radiation	MoK α (0.71069 Å)
Crystal size (μm)	$25 \times 30 \times 60$
Scan mode	ω
Scan width (°)	1.60
Scan speed (°/min)	0.78
Range of hkl	-9,9 -9,9 0,8
R_{symm} (%)	2.6
No. of independent reflections	655
N_{obs}	395
No. of refined parameters	73
R_{obs} (%)	3.39

Note: $R_{\text{symm}} = (\sum \{N \sum [w(F_o - F_c)^2]\} / \sum [(N - 1) \sum (wF_o^2)])^{1/2}$; N_{obs} = number of reflections with $F_o > 4\sigma F_c$; $R_{\text{obs}} = \sum (w^2 |F_o - F_c|) / \sum (w^2 F_o)$.

were taken from the *International Tables for X-ray Crystallography*, volume IV (Ibers and Hamilton, 1974). The refinement was performed using the program SHELX (Sheldrick, 1976).

Experimental details are reported in Table 1. The atomic coordinates and anisotropic displacement parameters are given in Tables 2 and 3, respectively, and a list of observed and calculated structure factors appears in Table 4.¹

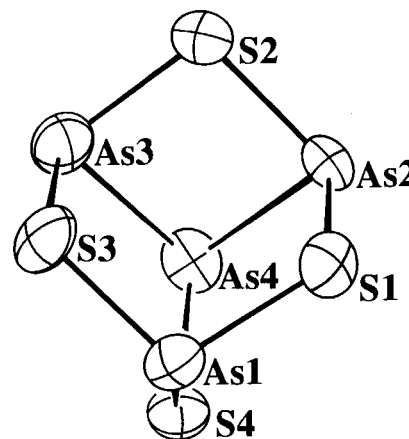
DISCUSSION

The pararealgar structure consists of discrete covalently bonded As₄S₄ molecules, which are held together by van der Waals forces. In the unit cell there are four such molecules. All the atoms lie in general positions (point symmetry 1); however, on the whole, the molecule (Fig. 1) shows a pseudomirror running through S2, As4, As1, and S4. Deviations from mirror symmetry, in terms of interatomic distances and angles, are <0.05 Å and 2.5°, respectively. Vibrational ellipsoids also display deviations from mirror symmetry. The As atoms show three

¹ A copy of Tables 3 and 4 may be ordered as Document AM-95-581 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 2. Fractional atomic coordinates and isotropic displacement parameters for pararealgar

Atom	x	y	z	U_{eq}
As1	0.3187(3)	0.6355(3)	0.0432(4)	0.038(1)
As2	0.0819(3)	0.5427(3)	0.3252(4)	0.035(1)
As3	0.3698(3)	0.3607(4)	0.3431(4)	0.050(1)
As4	0.1455(3)	0.3439(3)	0.1643(4)	0.041(1)
S1	0.1645(8)	0.7187(8)	0.1923(10)	0.040(3)
S2	0.2537(9)	0.4782(9)	0.5099(10)	0.046(4)
S3	0.4703(7)	0.5276(10)	0.2192(10)	0.052(4)
S4	0.1964(8)	0.4483(8)	-0.0492(10)	0.042(3)


Fig. 1. The As₄S₄ molecule in pararealgar. Vibrational ellipsoids are scaled at 50% probability.

different crystal chemical environments: As1 links three S atoms (S1, S3, S4); As2 and As3 each link two S atoms and one As atom (S1, S2, As4 and S2, S3, As4, respectively); As4 links one S atom and two As atoms (S4, As2, As3). The pararealgar molecule therefore differs from both

TABLE 5. Selected interatomic distances (Å) and angles (°) for pararealgar

Intramolecular bond distances			
As1-S1	2.254(9)	As2-As4	2.484(4)
-S3	2.238(8)	As3-S2	2.244(10)
-S4	2.261(8)	-S3	2.228(10)
As2-S1	2.251(9)	-As4	2.534(4)
-S2	2.252(9)	As4-S4	2.190(9)
Intramolecular bond angles			
S1-As1-S3	103.6(3)	S3-As3-As4	100.0(3)
S1-As1-S4	96.2(3)	S4-As4-As2	101.7(2)
S3-As1-S4	98.3(3)	S4-As4-As3	101.0(3)
S1-As2-S2	105.5(3)	As2-As4-As3	83.4(1)
S1-As2-As4	100.0(3)	As1-S1-As2	109.2(4)
S2-As2-As4	87.0(3)	As2-S2-As3	95.9(4)
S2-As3-S3	103.2(4)	As1-S3-As3	110.5(3)
S2-As3-As4	86.0(3)	As1-S4-As4	104.4(4)
Intramolecular nonbonded distances			
As1-As2	3.672(5)	As4-S2	3.266(9)
-As3	3.670(5)	-S3	3.652(8)
-As4	3.519(4)	S1-S2	3.586(12)
As2-S4	3.629(9)	-S3	3.530(11)
-As3	3.338(4)	-S4	3.361(12)
As3-S4	3.652(9)	S2-S3	3.506(12)
As4-S1	3.630(8)	S3-S4	3.404(11)
Intermolecular distances			
As1-S1 ^a	3.473(6)	As3-S3 ^g	3.653(10)
-S2 ^a	3.789(7)	-S4 ^b	3.618(9)
-S3 ^b	3.607(9)	As4-S1 ^f	3.652(9)
-As3 ^c	3.799(4)	-S2 ^c	3.592(9)
As2-S2 ^d	3.775(10)	-S4 ^b	3.720(9)
-S4 ^a	3.388(8)	S1-S2 ^a	3.478(10)
-As2 ^d	3.657(5)	S2-S3 ^b	3.345(11)
-As4 ^f	3.687(4)	S3-S4 ^b	3.777(11)

Note: the superscripts denote the symmetry and translation operations applied: a = +x, ½ - y, -½ + z; b = -x + 1, -y + 1, -z; c = -x + 1, +y + ½, -z + ½; d = -x, -y + 1, -z + 1; e = -x, -y + 1, -z; f = -x, +y - ½, -z + ½; g = -x + 1, +y - ½, -z + ½; h = +x, -y + ½, +z + ½; i = +x, -y + ½, +z - ½; j = -x + 1, -y + 1, -z + 1.

TABLE 6. X-ray powder diffraction pattern of pararealgar

Vancouver Island*		Present work**		
l/l_0	d_{meas} (Å)	d_{calc} (Å)	l/l_0	hkl
		9.8289	8	100
		6.8878	3	110
		6.3515	3	011
91	5.56	5.5834	83	111
100	5.14	5.1164	100	111
29	4.90†	4.9145	20	200
		4.8275	16	020
		4.1896	7	021
		3.9448	3	121
		3.8642	4	012
		3.7693	17	121
78	3.75	3.7477	48	112
		3.7186	16	211
		3.7084	8	102
		3.4618	5	112
27	3.44	3.4439	4	220
		3.4219	5	202
50	3.299	3.2924	67	221
		3.2253	3	212
3	3.184	3.1758	<3	022
		3.1025	3	310
33	3.105	3.0935	27	221
		3.0322	13	311
51	3.025	3.0166	28	202
		3.0068		
		2.9408	15	031
30	2.905	2.9124	9	122
		2.8793	26	131
		2.8793	11	212
		2.8396	3	131
		2.8046	28	311
71	2.795	2.7917	52	222
		2.6990	9	013
		2.6560	8	312
		2.6181	6	231
18	2.525†	2.5236	9	132
		2.4572	8	400
28	2.445	2.4414	13	302
		2.4306	5	132
		2.4209	3	123
		2.3977	6	322
		2.3813	4	410
11	2.377	2.3669	7	312
		2.3441	3	140
		2.3206	9	041
30	2.278	2.2793	15	223
		2.2763	4	141
		2.2528	2	213
		2.2201	3	313
11	2.208	2.2009	3	232
		2.1899	3	420
2	2.106†	2.1117	6	133
		2.0962	3	332
6	2.069	2.0636	14	421
		2.0333	6	204
22	2.030†	2.0302	22	133
		2.0157	3	233
		2.0147	6	402
		2.0098	2	104
		1.9724	4	242
16	1.976	1.9688	5	313
		1.9676	4	114
		1.9530	5	430
		1.9433	4	340
11	1.862	1.8611	9	333
		1.8407	3	512
		1.7972	3	250
6	1.744†	1.7443	10	152
		1.7309	5	224
		1.7219	3	440
		1.7159	3	413
		1.7127	4	152
10	1.710	1.7110	11	404
		1.7055	5	333
11	1.682†	1.6805	13	531

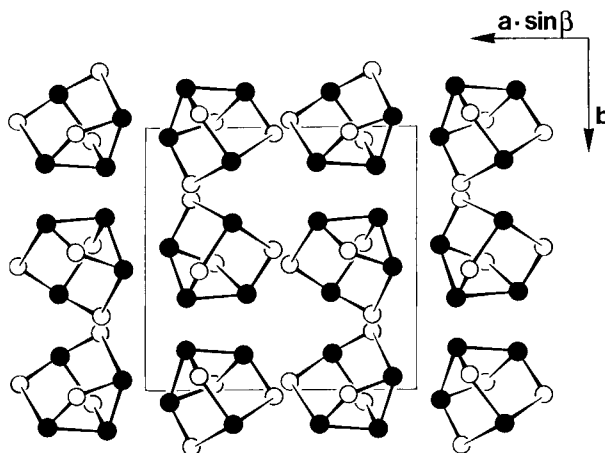


Fig. 2. The structure of pararealgar projected along [001]. As atoms are shown as solid circles and S atoms as open circles.

α -As₄S₄ (realgar) and β -As₄S₄, in both of which all four As atoms are bonded to 1As + 2S, but the molecule is the same as that found by Kutoglu (1976) for As₄S₄(II). Interatomic distances and angles are reported in Table 5. As-S bond distances are in the range 2.228–2.261 Å, except for As4-S4, which is only 2.190 Å. As-As bond distances range from 2.484 to 2.534 Å. These values agree closely with those reported for As₄S₄(II) (Kutoglu, 1976), α -As₄S₄ (Mullen and Nowacki, 1972), and β -As₄S₄ (Porter and Sheldrick, 1972).

Figure 2 shows the projection of the pararealgar structure down [001]. In this view the pararealgar structure appears similar to the [100] projection of As₄S₄(II) shown in Figure 3, though the difference in molecular packing is evident. In Table 5 intermolecular contacts shorter than 3.85 Å are reported. This limit corresponds to that adopted by Mullen and Nowacki (1972) for realgar on the basis of the sum of the van der Waals radii of As and S given by Pauling (1960), though the radii given by Bondi (1964) give a limiting value of 3.65 Å. The shortest contacts found in this study are As2-S4^e = 3.388 Å and S2-S3ⁱ = 3.345 Å; similar values are found in As₄S₄(II) and in realgar.

Table 6 compares the calculated X-ray powder pattern for the pararealgar used in this study with that observed for natural pararealgar from Vancouver Island (Roberts et al., 1980). The calculated and observed data match closely.

As a final observation, it may be pointed out that, because they have identical molecular weights and Z values, the densities of realgar and pararealgar should be very similar. Since the unit-cell volume of pararealgar (806.8

* X-ray powder data for pararealgar from Mount Washington Cu deposit, Comox district, Vancouver Island (Roberts et al., 1980).

** X-ray pattern calculated using XPOW software, version 2.0 (Downs et al., 1993). Only reflections with $l/l_0 > 2$ are listed.

† Indexing different from that of Roberts et al. (1980).

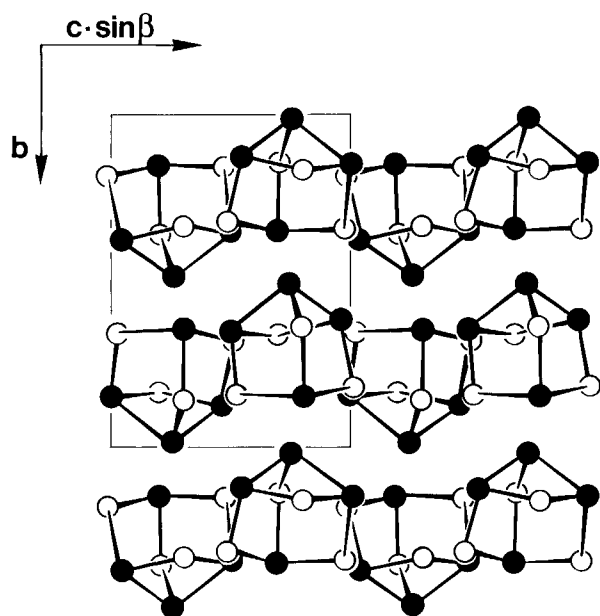


Fig. 3. The structure of $\text{As}_4\text{S}_4(\text{II})$ projected along [100]. As atoms are shown as solid circles and S atoms as open circles.

\AA^3) is somewhat greater than that of realgar (799.7 \AA^3), in the light-induced transformation of realgar to pararealgar the density decreases (realgar: $D_{\text{meas}} = 3.56$; $D_{\text{calc}} = 3.553$; pararealgar: $D_{\text{meas}} = 3.52$; $D_{\text{calc}} = 3.521$). Furthermore, it should be noted that, because of the different configuration of the As_4S_4 molecule in the two structures, some As-As and As-S bonds have to break during this process.

ACKNOWLEDGMENTS

The authors wish to thank the staff of the Mineralogical Museum of the University of Florence for providing the sample of realgar (no. 46768). The authors are also grateful to J.D. Grice and G. Robinson for their helpful reviews. Thanks are due to Johanna Krueger for reading the original manuscript. This study was funded by the C.N.R. and by M.U.R.S.T. (grant 60%).

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MANUSCRIPT RECEIVED JULY 18, 1994

MANUSCRIPT ACCEPTED NOVEMBER 7, 1994