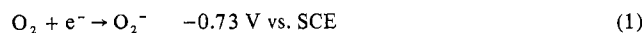


$10^{-6}$  M. The presence of two isobestic points (identical with those observed in the superoxide reaction) throughout the oxygenation demonstrated that no stable porphyrin intermediates or by-products were present.

### Discussion

Dioxygen is a very powerful four-electron oxidizing agent.<sup>1</sup> The one-electron reduction of  $O_2$ , however, is not a particularly favored reaction. The reduction potential for  $O_2$  in DMSO<sup>11</sup> demonstrates this fact:



Because dioxygen is a poor one-electron oxidizing reagent, superoxide is rarely found to be the product of oxidation of transition metal complexes by  $O_2$ . Instead it is more commonly found either that oxidations by  $O_2$  require the presence of protons as in the case of several Cu(I) complexes<sup>3,12</sup> or that oxidation occurs through a two-electron step where dioxygen obtains two electrons at once either from one metal<sup>13</sup> or by forming a binuclear  $\mu$ -peroxo species.<sup>14</sup>

Although the reduction of MnTPP<sup>+</sup> by superoxide in DMSO is quantitative, the oxygenation reaction of MnTPP in DMSO is clearly neither quantitative nor clean. Oxygenation of solutions of MnTPP in DMSO gives a 77% yield of MnTPP<sup>+</sup> and evidence for free Mn<sup>2+</sup> (from EPR). There is no evidence for superoxide as a product nor for stable peroxo or  $\mu$ -oxo intermediates. The results from the superoxide reaction allow us to rule out a one-electron oxidation resulting in the formation of superoxide. Thus the most likely mechanism is a two-electron oxidation occurring either through a  $\mu$ -peroxo intermediate or a mononuclear peroxo intermediate such as Mn<sup>IV</sup>TPP( $O_2^{2-}$ ).<sup>8</sup> Such peroxo species or peroxide,  $O_2^{2-}$ , itself are unlikely to be stable in DMSO since hydrogen peroxide,  $H_2O_2$ , reacts with DMSO.<sup>15,16</sup> It is also possible that some oxygenation of the porphyrin ligand is occurring perhaps catalyzed by MnTPP and resulting in the presence of free Mn<sup>2+</sup>. This might occur in DMSO where the reaction with  $O_2$  is slow and might not be observed in other solvents such as toluene where the oxidation is instantaneous at room temperature. In toluene, MnTPPpy is oxidized very rapidly by  $O_2$  with the stoichiometry  $O_2:Mn = 1:4$ .<sup>17</sup> Unfortunately, we cannot study the superoxide reaction in toluene or benzene because superoxide is not stable enough in these solvents to allow quantitative studies.<sup>18</sup>

In conclusion, observation of the quantitative reduction of MnTPP<sup>+</sup> by  $O_2^-$  in DMSO provides information pertaining to the mechanism of oxidation of MnTPP by  $O_2$  in the same solvent, a reaction that is itself difficult to study because of secondary reactions.

The product of the reaction of superoxide with MnTPP has not yet been identified. The possibility that this complex is  $[Mn^{II}TPP(O_2^-)]^-$  or  $[Mn^{III}TPP(O_2^{2-})]^-$  is under investigation.

**Acknowledgment.** Financial support from the Rutgers Research Council, the Charles and Johanna Busch Memorial Fund, a Biomedical Sciences Support Grant, the Research Corp., and the National Science Foundation is very gratefully acknowledged.

**Registry No.** MnTPP<sup>+</sup>, 59388-92-0; MnTPP, 31004-82-7;  $O_2^-$ , 11062-77-4.

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### Crystal Structure of Monoclinic Sulfur<sup>1</sup>

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Monoclinic sulfur is the form which is stable at normal pressure from 95 °C to the melting point (115 °C). Below 95 °C the orthorhombic form ("rhombic sulfur") is stable, but pure crystals of the metastable monoclinic form can be preserved for weeks at room temperature. Sands<sup>2</sup> determined the structure of the monoclinic crystals from photographic x-ray diffraction patterns and reported preliminary atomic coordinates, but the data were not accurate enough for good refinement.<sup>3</sup> In this paper we report more precise parameters, derived from diffractometer data, which confirm Sands' conclusion about the structure.

### Experimental Section

Crystals of monoclinic sulfur were produced accidentally by Dr. R. Gradl in an attempt to make a substituted diethiethene complex of uranium, and their identity was not recognized until one of them (a nine-faced crystal with dimensions about  $0.3 \times 0.3 \times 0.2$  mm mounted in a quartz capillary) was examined by x-ray diffraction. Unit cell dimensions were derived from the setting angles of 12 reflections (with  $40^\circ < 2\theta < 45^\circ$ ) measured with a Picker FACS-I diffractometer with a graphite monochromator and Mo radiation ( $\lambda$  0.70926 Å for  $K\alpha_1$ ). The same instrument was used to measure intensities using a  $\theta$ - $2\theta$  scan technique with a scanning rate of  $2^\circ/\text{min}$  from  $1^\circ$  below  $2\theta$  for  $K\alpha_1$  to  $1^\circ$  above  $2\theta$  for  $K\alpha_2$ . Background was counted for 4 s with an offset of  $0.5^\circ$  from each end of the scan. Three strong reflections (333, 060, 224) checked at intervals of 200 measurements indicated no decay within the accuracy of the experiment.

Absorption corrections calculated by an analytical integration<sup>4</sup> ranged from 1.338 to 1.808. Their validity was verified by multiple measurements of several reflections at various azimuthal angles.

Measurements were made of 4577 reflections not excluded by the space group in the hemisphere  $\pm h, k, \pm l$  and up to  $2\theta = 50^\circ$ . These reflections represent 2254 unique reflections; for 1627,  $F^2 > \sigma(F^2)$ ; and for 1140,  $F^2 > 3\sigma(F^2)$ .

**Crystal Data.** The space group is  $P2_1/c$ ; at 24 °C,  $a = 10.926$  (2),  $b = 10.855$  (2),  $c = 10.790$  (3) Å,  $\beta = 95.92$  (2)°,  $Z = 48$  atoms,  $d_x = 2.008$  g cm<sup>-3</sup>.

**Determination of the Structure.** The structure was solved with the MULTAN program,<sup>5</sup> to give an independent check of the previous work. With anisotropic thermal parameters (for the 16 atoms in the asymmetric unit) the full-matrix least-squares refinement reduced  $R_2 = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$ , the quantity minimized, to 0.030 and also  $R_1 = \sum |\Delta F| / \sum |F_o|$  to 0.030 for 1140 reflections with  $F^2 > 3\sigma(F^2)$ . We used  $\sigma^2(F^2) = s^2(F^2) + (0.035F^2)^2$ ;  $s^2(F^2)$  is the variance of  $F^2$  based on counting statistics or alternatively that based on the scatter of measurements of equivalent reflections when the latter exceeds 16 times the former. The factor 0.035 which reduced the effect of strong

Table I. Atomic Parameters and Esd's

Atom	$x^a$	$y$	$z$	$B_{11}^b$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
1	0.2333 (1)	0.5251 (1)	0.0299 (1)	4.70 (7)	3.85 (7)	4.89 (7)	0.57 (6)	0.17 (6)	0.63 (6)
2	0.1538 (1)	0.3555 (2)	0.0070 (1)	3.44 (6)	5.88 (8)	6.05 (8)	-1.00 (6)	-0.31 (6)	0.62 (7)
3	0.2572 (1)	0.2523 (1)	-0.1022 (1)	5.89 (8)	4.61 (7)	4.06 (7)	-0.69 (6)	-1.79 (6)	-0.32 (7)
4	0.3720 (1)	0.1439 (1)	0.0134 (1)	6.08 (8)	2.90 (6)	5.02 (7)	-0.82 (6)	-1.16 (6)	0.08 (6)
5	0.5398 (1)	0.2283 (1)	0.0381 (1)	4.25 (7)	3.87 (6)	3.46 (6)	0.43 (5)	0.20 (5)	-0.23 (5)
6	0.5531 (1)	0.3154 (1)	0.2075 (1)	4.65 (7)	4.08 (6)	2.89 (5)	-0.06 (6)	-0.79 (5)	0.24 (5)
7	0.5133 (1)	0.4979 (1)	0.1780 (1)	4.52 (7)	3.40 (6)	4.19 (6)	-0.94 (5)	0.02 (5)	-0.62 (5)
8	0.3317 (1)	0.5246 (1)	0.2023 (1)	5.35 (8)	4.48 (7)	3.79 (6)	0.05 (6)	0.92 (5)	-1.11 (6)
9	0.1783 (3)	-0.1083 (4)	0.0823 (4)	3.6 (2)	5.6 (2)	8.9 (3)	0.3 (1)	-1.5 (2)	0.7 (2)
10	0.0505 (4)	-0.0710 (4)	0.2039 (3)	7.6 (2)	6.7 (2)	5.4 (2)	-0.6 (2)	-1.3 (2)	2.8 (2)
11	0.0074 (4)	0.1125 (4)	0.1880 (3)	8.1 (3)	5.8 (2)	3.8 (2)	-0.2 (2)	-1.8 (2)	-0.8 (1)
12	-0.1553 (3)	0.1273 (4)	0.0790 (3)	4.6 (2)	6.3 (2)	4.6 (2)	0.7 (2)	1.2 (1)	-0.1 (2)
13	-0.1199 (3)	0.1709 (3)	-0.0981 (3)	5.1 (2)	4.5 (2)	4.3 (1)	0.4 (1)	-0.3 (1)	1.2 (1)
14	-0.1266 (3)	0.0105 (4)	-0.1966 (3)	4.9 (2)	7.8 (2)	4.1 (1)	-0.2 (2)	-1.0 (1)	-1.5 (2)
15	0.0510 (4)	-0.0466 (5)	-0.2030 (4)	5.5 (2)	8.1 (3)	5.7 (2)	-0.0 (2)	2.1 (2)	-1.3 (2)
16	0.0899 (4)	-0.1822 (4)	-0.0743 (4)	4.7 (2)	4.2 (2)	9.5 (3)	0.2 (1)	0.3 (2)	-1.3 (2)

<sup>a</sup> Estimated standard deviation of the last digit is enclosed in parentheses. <sup>b</sup> The form of the temperature factor is  $\exp[-0.25 (B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* + \dots)]$ .

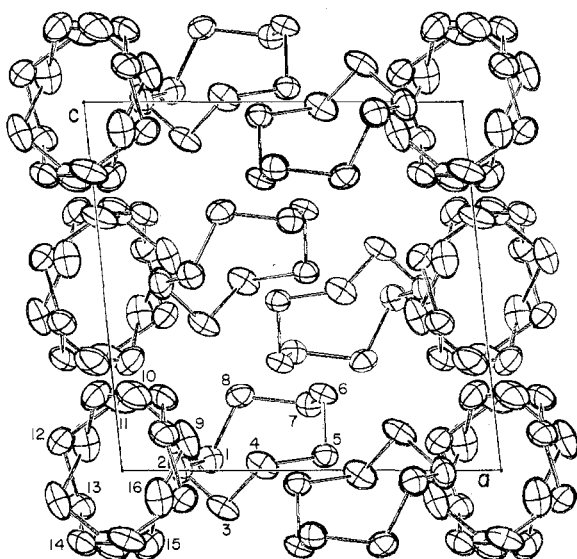


Figure 1. Structure of monoclinic sulfur, viewed up the  $b$  axis. Numbers designate the atoms listed in the tables. The two alternate positions for the disordered molecules are both shown.

reflections was chosen by trial and error to give a flat distribution of  $\langle w(\Delta F)^2 \rangle$  as a function of magnitude of  $F$ ,  $w = (\sigma(F))^{-2}$ , or zero for reflections weaker than  $3\sigma(F^2)$ . Scattering factors for neutral S were taken from Doyle and Turner<sup>6</sup> and the dispersion corrections from Cromer and Liberman.<sup>7</sup> The standard deviation of observation of unit weight was 0.998. In the last cycle, no parameter changed more than  $0.0002\sigma$ . Final parameters are listed in Table I.<sup>8</sup>

### Discussion

The structure (Figure 1) consists of crown-shaped  $S_8$  rings in two kinds of positions. Two-thirds of them (atoms 1-8) are in general positions without any disorder. The others (atoms 9-16) are located around centers of symmetry. The crown lacks centric symmetry, and the molecules gain this symmetry by disorder between two orientations, each occupied with 50% probability. The entropy of this disorder, if it is completely random, is  $(R/24) \ln 2 = 0.057$  eu/(g-atom). Montgomery<sup>9</sup> obtained  $0.007 \pm 0.020$  eu/(g-atom) for the residual entropy at low temperature relative to orthorhombic sulfur, and he discovered a lambda-type heat capacity anomaly (peaking at about 198 K) which is estimated to involve 0.05 eu/(g-atom) of extra entropy. An earlier check of the entropy by Eastman and McGavock<sup>10</sup> appears to have omitted some of the entropy of the lambda anomaly, but within its accuracy of 0.06 eu/(g-atom) it is in agreement with Montgomery's result. As pointed out by Montgomery, the entropy data imply the

Table II. Bond Distances (Å) with Esd's

Atoms	Distance	Atoms	Distance
1-2	2.040 (2)	9-10	2.053 (6)
2-3	2.048 (2)	10-11	2.050 (5)
3-4	2.047 (2)	11-12	2.034 (5)
4-5	2.042 (2)	12-13	2.044 (5)
5-6	2.050 (2)	13-14	2.038 (5)
6-7	2.047 (2)	14-15	2.045 (5)
7-8	2.048 (2)	15-16	2.038 (6)
8-1	2.050 (2)	16-9	2.024 (6)

Table III. Bond Angles (deg) with Esd's

Central atom	Angle	Central atom	Angle
1	106.5 (1)	9	108.3 (2)
2	108.1 (1)	10	107.7 (3)
3	107.7 (1)	11	107.7 (3)
4	107.9 (1)	12	108.7 (2)
5	107.7 (1)	13	106.8 (2)
6	108.2 (1)	14	107.1 (2)
7	108.1 (1)	15	109.1 (3)
8	108.0 (1)	16	109.3 (3)

disorder exists down to about 200 K but disappears gradually at lower temperatures. An ordered structure requires a change to lower symmetry of the crystal, with either a different space group or larger unit cell. The gradual nature of the transition makes it likely that the general molecular packing stays the same.

The bond distances (Table II) are all equal nearly to the estimated precision of the determination. A weighted average is 2.045 (1) Å. The bond angles (Table III), with a weighted average of 107.9 (1)°, range from 106.5 to 109.3°. It is plausible that this variation is the result of packing forces. These results are very similar to those reported by Abrahams<sup>11</sup> for  $S_8$  molecules in orthorhombic sulfur; average distance 2.037 (5) Å and average angle 107.8 (4)°.

Monoclinic sulfur exhibits twinning in which the directions of the  $a$  and  $b$  axes are interchanged,<sup>12</sup> and the molecular structure offers an explanation. Each of the atoms listed in Table I obeys the condition  $(x_1, y_1, z_1) = (y_2, x_2, z_2) + \Delta$ , with  $\Delta = 0.36$  Å or less, either with itself or with some other atom in the structure. This approximate mirror symmetry may be seen in Figure 2 as reflection across one of the diagonals of the cell, but it applies only to half of the molecules. The other half have similar approximate symmetry, but in another direction. The pseudosymmetry permits a molecule at the twin boundary to fit simultaneously into the two orientations of the structure. If the mirror pseudosymmetry extended to the whole structure, monoclinic sulfur would be a candidate for ferroelastic behavior. For the actual structure, a ferroelastic

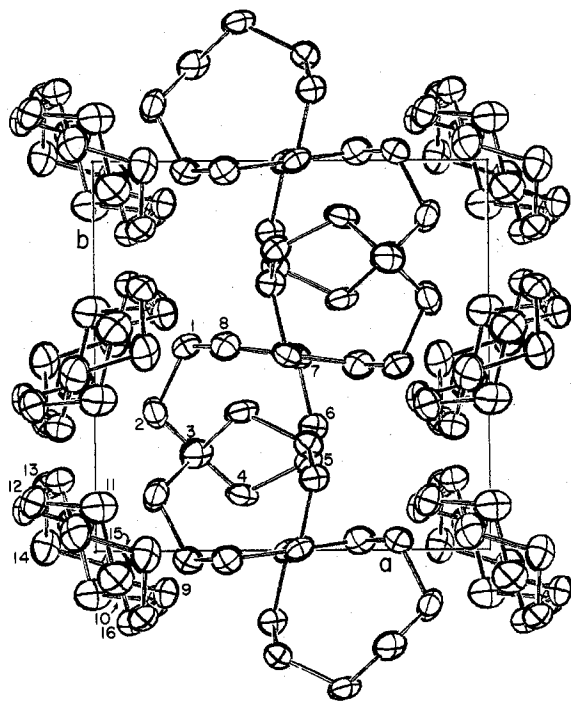


Figure 2. Structure viewed down the  $c$  axis. The numbered atoms are the same as in Figure 1.

interchange of  $a$  and  $b$  would require far greater molecular shifts than occur in the materials which are known to have this property.<sup>13</sup>

We thank a perceptive referee who noticed the special relationship among the coordinates.

Registry No. S<sub>8</sub>, 10544-50-0.

**Supplementary Material Available:** A listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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## Physical Properties of Linear-Chain Systems.

### 4. Optical Spectrum of RbMnBr<sub>3</sub><sup>1</sup>

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The compound RbMnBr<sub>3</sub> belongs to a class of compounds of general formulation ABX<sub>3</sub> which display predominantly one-dimensional magnetic character.<sup>2</sup> When A<sup>+</sup> = Cs<sup>+</sup>, Rb<sup>+</sup>, or (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>, B = a divalent first-row transition element, and

Table I. Observed Maxima, Octahedral Ligand Field Assignments, and Measured Oscillator Strengths in the Spectrum of RbMnBr<sub>3</sub> at 4.2 K

Obsd max, cm <sup>-1</sup>		Assignments (octahedral ligand field states)	Manifold oscillator strengths (f × 10 <sup>6</sup> )	
$E \parallel c$	$E \perp c$		$E \parallel c$	$E \perp c$
18 149	18 136	<sup>6</sup> A <sub>1</sub> (S) → <sup>4</sup> T <sub>1</sub> (G)	0.81	6.44
21 739	21 552		→ <sup>4</sup> T <sub>2</sub> (G)	7.18
22 995		→ <sup>4</sup> A <sub>1</sub> (G)		
23 063	23 059	→ <sup>4</sup> E(G)		
23 138		→ <sup>4</sup> A <sub>1</sub> + ν <sub>150</sub>	1.13	0.18
	23 199	→ <sup>4</sup> E + ν <sub>140</sub>		
23 283		→ <sup>4</sup> A <sub>1</sub> + 2ν <sub>150</sub>		
	23 337	→ <sup>4</sup> E + 2ν <sub>140</sub>		
23 364				
26 164	26 161	<sup>4</sup> T <sub>2</sub> (D)	2.41	8.05
~26 360	26 350			
	26 455			
26 504				
26 596	~26 585			
~27 370	27 365	→ <sup>4</sup> E(D)		
	~27 410			
~27 500	27 510	→ <sup>4</sup> E(D) + ν <sub>145</sub>	0.12	2.44
	~27 555	→ <sup>4</sup> E(D) + 2ν <sub>145</sub>		
~27 650	27 655	→ <sup>4</sup> T <sub>1</sub> (P)	0.37	1.05
29 498				
29 638	29 640			
~29 890	~29 900			
30 030	30 030			
34 602	~34 600	→ <sup>4</sup> A <sub>2</sub> (F)		

X<sup>-</sup> = Cl<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>, these materials crystallize in a hexagonal array of infinite linear chains which are composed of face-sharing BX<sub>6</sub><sup>4-</sup> octahedra and lie parallel to the  $c$  crystallographic axis. The chains are separated from one another by the A cations and this separation effectively inhibits interchain exchange. Three-dimensional ordering occurs only at low temperatures while one-dimensional spin correlation is evident at temperatures far above the temperature limit of three-dimensional order.<sup>3-5</sup> The unique nature of these materials is also manifested spectroscopically.<sup>6-8</sup> The absorption spectra exhibit anomalous intensity of spin-forbidden transitions and dependence on temperature incommensurate with that expected for vibronic coupling.

To further analyze the properties of these compounds we have measured the polarized, single-crystal absorption spectrum of RbMnBr<sub>3</sub> from 300 to 4.2 K.

## Experimental Section

Single crystals suitable for spectroscopic measurements were prepared as previously described<sup>6</sup> employing anhydrous RbBr and MnBr<sub>2</sub> as starting materials. Polarized spectroscopic measurements were also obtained as before and were made at 300, 150, 120, 100, 80, 60, 40, 30, 20, 15, and 4.2 K. Comparison of  $\sigma$ ,  $\pi$ , and axial results showed all observed transitions to be electric dipole in nature. RbMnBr<sub>3</sub> was determined to be isomorphous and isostructural with the linear-chain material CsMnBr<sub>3</sub> by x-ray photographic techniques.<sup>10</sup>

## Results and Discussion

The polarized absorption spectrum of RbMnBr<sub>3</sub> at 4.2 K is presented in Figure 1. The gross features of the spectrum can be understood in terms of transitions between the octahedral ligand field states of Mn<sup>2+</sup>. Assignments on this basis are given with the spectrum in Figure 1. Table I contains the energies of the observed maxima and the oscillator strengths of the absorption manifolds at 4.2 K. Figure 2 presents the variation of oscillator strengths with temperature for those bands which were sufficiently isolated throughout the measured temperature range to permit accurate measurement. The oscillator strengths are normalized with respect to the 4.2-K value. This facilitates comparison between