Crystal Structure of (18 – Crown – 6.K)₂K[(Co(OH)₆Mo₆O₁₈]·12H₂O

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Structural Characterization of Crown Ether Complexed Potassium Ion $(C_{12}H_{24}O_6 \cdot K)_2K[Co(OH)_6Mo_6O_{18}] \cdot 12H_2O$

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The crystal structure of $(C_{12}H_{24}O_6 \cdot K)_2K[Co(OH)_6Mo_6O_{18}] \cdot 12H_2O$ has been determined by X-ray diffraction. Crystal data as fallows; monoclinic, space group C_2/m, $a = 22.512(4)$ Å, $b = 18.304(4)$ Å, $c = 7.641(1)$ Å, $\beta = 90.52(2)$ Å, and $Z = 2$. A final conventional R value of 0.044 was obtained by least-squares refinement of 4173 independent observed $[|Fo| \geq 3\sigma(|Fo|)]$ reflections. The $[Co(OH)_6Mo_6O_{18}]^{-3}$ polyanion shows the well-known Anderson-structure and has approximate $3m$ symmetry. A $[Co(OH)_6Mo_6O_{18}]^{-3}$ polyanion is located between two crown ether complexed cations forming a sandwich structure. One potassium ion interacts with the crown ether *via* electrostatic interactions. The other potassium ion only interacts with the water molecules and terminal oxygen atoms of the polyanion.

Introduction

Crystals of polyoxometalate salts often contain much water of crystallization. Therefore, the crystals occasionally are not stable during X-ray work because of release of the water molecules. The crown ether complexed ion as counter cation was used in order to obtain X-ray quality crystalline samples. The successful results were reported by authors.[1-3] The heteropolyanion of Anderson-structure, $[X^{+n}Mo_6O_{24}]^{-(12-n)}$(X: heteroatom) is similar to the 18-crown-6 complexed cation in its size and shape, so that the stable packing in a crystal lattice can be anticipated in the arrangement of both polyanion and complexed cation. In this paper we report the structure of the $(18$-Crown-$6.K)_2K[Co^{III}(OH)_6Mo_6O_{18}] \cdot 12H_2O$ which is Anderson-structure heteropolyanion having lower oxidation state heteroatom.

Experimental

Crystals of $(18$-Crown-$6.K)_2K[Co(OH)_6Mo_6O_{18}] \cdot 12H_2O$ were prepared as fallows. A solution of 0.05 mol of $Co(NO_3)_2 \cdot 6H_2O$ and 10 ml of 35% H_2O_2 in 40 ml of water was added dropwise with stirring the slurry, cooled by a dry ice-ethanol bath(-5 °C), of 1.0 mol of K_2CO_3 in 100 ml of water. The mixture was stirred for one hour at -5 °C and filtered off rapidly.

The olive-green filtrate was added to the solution cooled at 0 °C of 0.03 mole of $(NH_4)_7[Mo_7O_{24}] \cdot 4H_2O$ in 500 ml of water. The mixture was stirred for three hours under 10 °C, a dark-green material was precipitated gradually. The precipitate was solved in 350 ml of water at room temperature and filtered off, an excess of KCl was added to the filtrate, a sordid-green precipitate was deposited immediately; the precipitate changes from sordid-green to emerald-green by the repetition of this procedure. Recrystallization of the emerald-green product from an aqueous solution gave the crystal of $K_3[Co(OH)_6Mo_6O_{18}] \cdot 7H_2O$. However, it is difficult to obtain the suitable crystals for the structure determination. The solution of 0.018 mol of 18-crown-6 added to the solution of 0.006 mol of $K_3[Co(OH)_6Mo_6O_{18}] \cdot 7H_2O$. The mixed solution was allowed to stand for three weeks, the suitable crystals of $(C_{12}H_{24}O_6 \cdot K)_2K[Co(OH)_6Mo_6O_{18}] \cdot 12H_2O$ for X-ray study were obtained.

A summary of crystal data, together with the details concerning intensity measurements is given Table 1. Intensities of standard reflections no significant changes were observed the period of data collection. The data were corrected for the Lorentz and polarization effects. Neither absorption nor extinction corrections were applied. Calculations carried out with *UNICS*[4] on the 8800/8870 computer at the *Computer Center of the University of Tokyo*. The final atomic and aniso-

Table 1. Summary of Crystal Data, Intensity Collection and Least-Squares Refinement Stactistics

formula	$(C_{12}H_{24}O_6 \cdot K)_2K[Co(OH)_6Mo_6O_{18}] \cdot 12H_2O$
fw	1886.73
space group	monoclinic, $C2/m$
a, Å	22.512(4)
b, Å	18.304(4)
c, Å	7.641(1)
β, deg.	90.52(2)
V, Å^3	3148.6(9)
Z	2
μ(Mo K), cm^{-1}	17.05
density, gcm^{-3}	1.99(calc.) 2.01(meas.)
radiation	Mo K$_\alpha$(graphite monochrom, $\lambda = 0.7107$Å)
crystal size, mm	sphere, $\phi = 0.36$ mm
cell-constant determination	25 reflections (35° 2 45°)
reflection measured	$\pm h$ max. 31, $+k$ max. 18, $+l$ max. 9
2θ range, deg.	3–60°
scan type	ω–2θ
scan speed, deg. min.$^{-1}$	1.0
scan range, deg.	$2\theta(1.1° + 0.2°\tan$)
standard reflection	3/80 min.
No. of unique reflection	4173 $|Fo| \geq 3\sigma(|Fo|)$
R	0.044
wR	0.045
w^{-1}	$1/\sigma(|Fo|)$
(Δ/σ)max.	0.008
final p excursions (eÅ^{-3})	12(the maximum values are near Mo atom)
diffractometer	Philips

Table 2. Fractional Coordinates (and Estimated Standard Deviations) of the non-Hydrogen Atoms (Values are $\times 10^4$)

Atom	x	y	z
Co	0	0	0
Mo(1)	0	1815(1)	0
Mo(2)	1239(1)	902(1)	930(1)
Oc(1)	813(2)	0	−740(5)
Oc(2)	249(2)	781(2)	1519(4)
Ob(1)	1277(2)	0	2258(5)
Ob(2)	807(2)	1537(2)	−642(4)
Ot(1)	136(2)	2381(2)	1737(4)
Ot(2)	1374(2)	1468(2)	2674(4)
Ot(3)	1885(2)	850(2)	−198(5)
K(1)	2905(1)	0	8958(2)
O(1)	2638(5)	617(8)	5553(9)
O(2)	3128(4)	1436(5)	7742(16)
O(3)	3706(5)	844(9)	10797(11)
C(1)	2638(4)	483(7)	4291(11)
C(2)	2647(7)	1463(8)	5738(20)
C(3)	2854(6)	1885(5)	7686(18)
C(4)	3344(7)	1874(4)	9669(16)
C(5)	3880(7)	1410(8)	10950(15)
C(6)	4248(4)	455(9)	11368(16)
K(2)	0	3037(2)	5000
H$_2$O(1)	0	981(4)	5000
H$_2$O(2)	1218(3)	0	5934(7)
H$_2$O(3)	4242(3)	781(4)	6283(9)
H$_2$O(4)	929(3)	2030(4)	5810(6)

Table 3. Anisotripic Thermal Parameters (Å^2) of the $\exp[-2\ 2$ $(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ form (Values are $\times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	22(1)	19(1)	20(1)	0	2(1)	0
Mo(1)	31(1)	20(1)	31(1)	0	3(1)	0
Mo(2)	24(1)	25(1)	34(1)	−3(1)	1(1)	−2(1)
Oc(1)	28(2)	24(2)	26(2)	0	5(2)	0
Oc(2)	28(2)	26(2)	24(2)	1(1)	4(1)	−2(1)
Ob(1)	36(2)	28(2)	29(2)	0	−7(2)	0
Ob(2)	29(2)	28(2)	34(2)	−2(1)	5(1)	4(1)
Ot(1)	45(2)	35(2)	46(2)	−5(2)	5(2)	−12(2)
Ot(2)	46(2)	37(2)	47(2)	−4(2)	−10(2)	−9(2)
Ot(3)	39(2)	42(2)	59(2)	−3(2)	12(2)	2(2)
K(1)	38(1)	35(1)	59(1)	0	1(1)	0
O(1)	205(10)	506(21)	83(5)	108(11)	−2(6)	−9(8)
O(2)	171(8)	140(7)	487(17)	85(6)	188(10)	199(10)
O(3)	230(10)	537(20)	164(7)	−306(12)	90(7)	−178(10)
C(1)	89(6)	284(16)	86(5)	−34(7)	−28(5)	95(8)
C(2)	252(18)	165(12)	272(17)	124(12)	20(14)	131(13)
C(3)	174(11)	64(6)	255(14)	31(7)	39(10)	32(8)
C(4)	249(16)	118(10)	165(10)	16(10)	−9(10)	−81(9)
C(5)	293(18)	202(13)	147(9)	−202(14)	66(10)	−93(9)
C(6)	56(5)	334(24)	194(11)	−43(8)	−36(7)	40(12)
K(2)	59(2)	47(2)	30(2)	0	−3(2)	0
H$_2$O(1)	100(5)	89(5)	35(3)	0	14(3)	0
H$_2$O(2)	56(4)	256(12)	34(3)	0	10(3)	0
H$_2$O(3)	95(5)	161(7)	122(5)	16(5)	−1(4)	−24(5)
H$_2$O(4)	120(5)	117(5)	55(3)	43(4)	21(3)	7(3)

tropic thermal parameters are given in Table 2 and 3.* The structure was solved by conventional heavy-atom method; Co and Mo atoms were located from three-dimensional Patterson maps, remaining atoms (without H atom) from successive difference Fourier maps; structure refined by block-diagonal least squares based on F with anisotropic thermal parameters for all atoms the non-hydrogen atoms; atomic scattering factors from *International Table for X-ray Crystallography*[5] including f' and f'' for Co and Mo.

Result and Discussion

Anderson-structure heteropolyanions, $[X^{+n}Mo_6O_{24}]^{-(12-n)}$ (X:heteroatom) showed two interesting behaviors in the crystal system. One is protonation of the polyanion, and the other is its geometrical isomerization.[6,7] The hexamolybdopolyanions having heteroatom with higher oxidation states such as $[Te^{VI}Mo_6O_{24}]^{-6}$ [8] and $[I^{VII}Mo_6O_{24}]^{-5}$ [9] do not contain

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*The final *Fo–Fc* tables (total 28 pp) are available as supplementary materials from U. Lee.

Crystal Structure of (18 - Crown - 6.K)₂K[(Co(OH)₆Mo₆O₁₈]·12H₂O
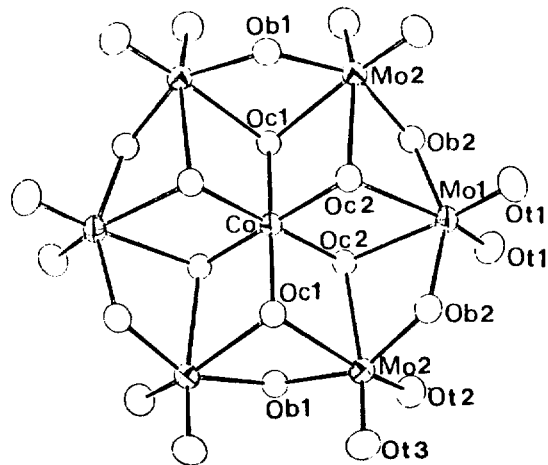
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Figure 1. The structure of the $[Co(OH)_6Mo_6O_{18}]^{-3}$ polyanion. (Except for H toms).

Table 4. Interatomic Distances and Angles in the $[Co(OH)_6Mo_6O_{18}]^{-3}$

Distances (Å)		Distances (Å)	
Co	–Mo(1) 3.311(1)	Mo(2)–Oc(1)	2.292(2)
	–Mo(2) 3.322(1)	–Oc(2)	2.287(3)
	–Oc(1) 1.920(3)	–Ob(1)	1.939(2)
	–Oc(2) 1.922(2)	–Ob(2)	1.929(3)
		–Ot(2)	1.713(3)
		–Ot(3)	1.701(3)
Mo(1)–Mo(1)ⁱ 3.301(1)			
Mo(2) 3.322(1)			
Oc(2) 2.287(2)			
Ob2(2) 1.952(3)			
Ot(1) 1.709(3)			

Angles (°)	
Mo(1)–Co–Mo(2)	60.10(1)
Mo(1)–Co–Mo(1)ⁱ	59.80(1)
Oc(1)–Co–Oc(1)ⁱ	96.1(2)
Oc(1)–Co–Oc(2)	84.5(2)

symmetry code: *i*: *x*, –*y*, *z*.

Table 5. The Comparison of Interatomic Distances in $[Co(OH)_6Mo_6O_{18}]^{-3}$ and $[Cr(OH)_6Mo_6O_{18}]^{-3}$ Polyanion (X: Heteroatom)

Anion	$[Co(OH)_6Mo_6O_{18}]^{-3}$		$[Cr(OH)_6Mo_6O_{18}]^{-3}$	
	Average distance (Å)	Range (Å)	Average distance (Å)	Range (Å)
X –Mo	3.317(1)	3.311–3.322	3.32(2)	3.303–3.349
Mo–Mo	3.310(10)	3.301–3.322	3.33(2)	3.309–3.351
X –Oc	1.921(3)	1.920–1.922	1.975(8)	1.968–1.972
Mo–Oc	2.289(3)	2.287–2.292	2.29(3)	2.243–2.347
Mo–Ob	1.940(9)	1.929–1.952	1.94(2)	1.907–1.985
Mo–Ot	1.708(5)	1.701–1.713	1.709(9)	1.695–1.720

non–acidic hydrogen atom. But, the one with lower oxidation state carries six non-acidic protons attached to oxygen atoms in the central XO_6 octahedron such as $[Cr^{III}(OH)_6Mo_6$-

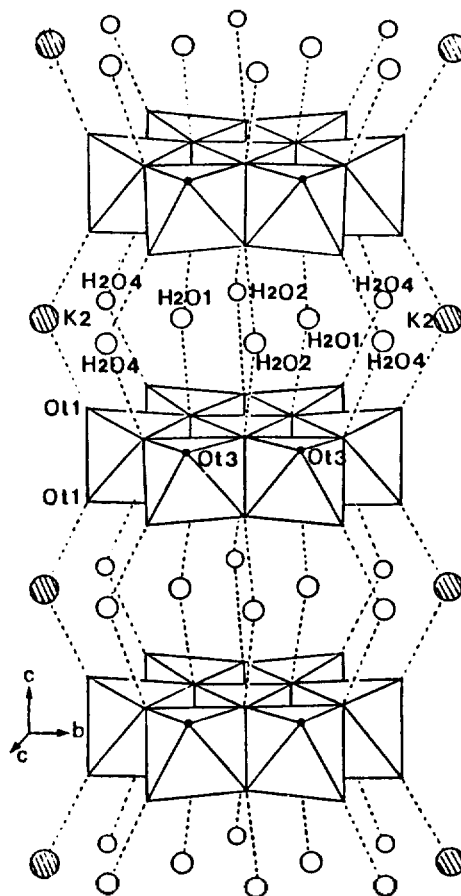**Figure 2.** Interactions between polyanions by water molecules and $K^+(2)$ The Ot(3) atoms interact with $K^+(1)$.

$O_{18}]^{-3}$ [10] and $[Cu^{II}(OH)_6Mo_6O_{18}]^{-4}$ [11]. The polyanion, $[Co^{III}(OH)_6Mo_6O_{18}]^{-3}$ containing lower oxidation state, Co^{III} heteroatom also has about D_{3d} ($\bar{3}m$) symmetry. The configuration of the polyanion is shown in Figure 1. The $[Co(OH)_6Mo_6O_{18}]^{-3}$ polyanion consists of a ring of six distorted MoO_6 octahedron surrounding one Co atom. Six Mo atoms around Co atom form a neary planar hexagon of approximately 3.32 Å. Oxygen atoms in the anion may be divided into three groups, Oc, Ob and Ot, where Ot is the terminal O atom bound to a Mo atom, Ob is the bridging atom between two Mo atoms, and Oc is the central atom which coordinate to the Co and Mo atoms. Table 4 lists bond lengths and angles in the anion. The Mo–O distances fall into three ranges which depend on the group of coordinated oxygen atom. The Mo–Oc distances are between 2.287 Å and 2.292 Å. The Mo–Ob distances range from 1.929 Å to 1.952 Å. The Mo–Ot length lie between 1.701 Å and 1.731 Å. A similar tendency has been found in other hexamolybdoheteropoly anions.[8,9] The average bond distances compare with the isostructure polyanion, $[Cr(OH)_6Mo_6O_{18}]^{-3}$ [10] in the Table 5. The bond distances of Mo–Oc, Mo–Ob and Mo–Ot are very close. But, Co–Mo, Mo–Co and Co–Oc distances are shorter than those of [Cr(OH)₆Mo₆O₁₈]⁻³ polyanion. These differences can be explained by the ionic radii of heteroatoms. The effective ionic radii of the Co^{III} is 0.687 Å (low spin, 6 coordinated value) and Cr^{III} is 0.755 Å (6 coordinated value).[12] The X–Oc (X:heteroatom) bond distance very affect for the Mo–Mo and X–Mo distan-

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Table 6. K$^+$-O Distances and Probable Hydrogen Bond Distances (<3.0 Å)

		Distance (Å)			Distance (Å)
K(1)	-O(1)	2.895(8)	K(2)	-Ot(1)	2.787(3)
	-O(1)^i	2.895(8)		-Ot(1)^{iv}	2.787(3)
	-O(2)	2.834(8)		-H$_2$O(3)^v	2.929(7)
	-O(2)^i	2.834(8)		-H$_2$O(3)^{vi}	2.929(7)
	-O(3)	2.751(11)		-H$_2$O(4)	2.850(6)
	-O(3)^i	2.751(11)		-H$_2$O(4)^{iv}	2.850(6)
	-Ot(3)^{ii}	2.851(3)			
	-Ot(3)^{iii}	2.851(3)			
H$_2$O(1)	-Oc(2)	2.748(3)	H$_2$O(3)-H$_2$O(3)^{iv}		2.857(15)
	-Oc(2)^{iv}	2.748(3)		-K(2)^v	2.929(7)
	-H$_2$O(4)	2.901(7)	H$_2$O(4)-Ob(2)^{ii}		2.873(5)
	-H$_2$O(4)	2.901(7)		-Ot(2)	2.803(5)
H$_2$O(2)	-Ob(1)	2.813(6)		-H$_2$O(1)	2.901(7)
	-Oc(1)	2.708(6)		-K(2)	2.850(6)

Symmetry code: i: x, $-y$, z. ii: x, y, $1+z$. iii: x, $-y$, $1+z$. iv: $-x$, y, $1-z$. v: $1/2-x$, $1/2-y$, $1-z$. vi: $-1/2+x$, $1/2-y$, z.
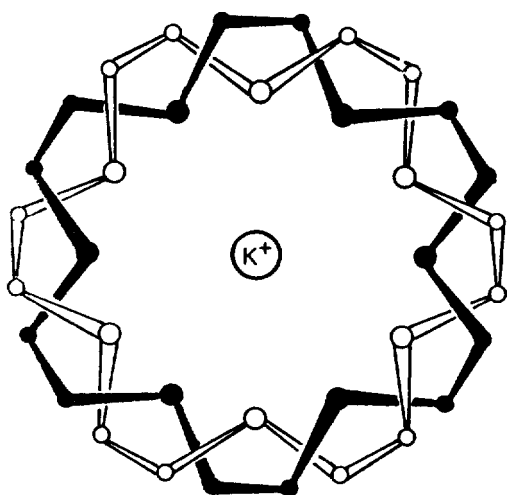
Figure 3. Disorder described in terms of two sites rotated *ca.* 30° with respect to each other around the approximate three fold axis of rotation.

Figure 4. The Crystal structure of (C$_{12}$H$_{24}$O$_6$.K)$_2$K[Co(OH)$_6$Mo$_6$-O$_{18}$].12H$_2$O projected on the (001) plane.

ces. The same case is shown in the [Pt^{IV}W$_6$O$_{24}$]$^{-8}$ [13] and [Mn^{IV}W$_6$O$_{24}$]$^{-8}$ [14] polyanions.

Elemental analysis suggest that six hydrogen atoms as non acidic protons must be included in the present complex. Although the positions of these hydrogen atoms could not be detected on the difference Fourier maps, the most likely sites of the hydrogen atoms are on the six Oc atoms in the anion. The arguments about the position of hydrogen atoms had been discussed in the crystal structure study of Na$_3$[Cr(OH$_6$-Mo$_6$O$_{18}$].8H$_2$O.[10] Figure 2 shows the interaction of inter poly-anion by hydrogen bonds and ion-dipole interaction. The K$^+$-O distances and probable hydrogen bond distances are given in Table 6. Each of six Oc atoms interacts with two water molecules. The OcH--OH$_2$ distances (average 2.75 Å) are shorter than those of usual hydrogen bonds for water molecules. This fact suggests the presence of strong OcH--H$_2$O--HOc interactions between neighboring anions. The

anions are linked one after another by strong hydrogen bond (OcH--H$_2$O--HOc, OcH--H$_2$O--Ob and Ob--H$_2$O--Ot) and ion-dipole interaction (Ot--K--Ot). Potassium ion forming crown ether complexed cation, K$^+$(1), is disordered in two sites on the twofold axis of rotation; the two sites are crystallographically equivalent and surround by six oxygen atoms in the crown ether and two Ot atoms in the same poly-anion. K$^+$(2) is coordinated by four water molecules and two Ot atoms in the different anions.

The 18-crown-6 molecule has approximate D_{3d} but bond distances bond angles, and thermal parameters in the (18-Crown-6.K)$_2$K[Co(OH)$_6$Mo$_6$O$_{18}$].12H$_2$O molecule indicate a disordered structure. Several bond distances and angles in the 18-membered ring are unreasonable, and the thermal parameters of the crown molecule in the present complex are much larger than those in (18-Crown-6.K)$_2$MoO$_4$.5H$_2$O[1], (18-Crown-6.K)$_2$Mo$_6$O$_{19}$.H$_2$O[2] and (18-Crown-6.K)$_4$[CW$_{12}$-O$_{40}$].2H$_2$O. In the course of refinement we found that the electron densities for the atoms in question extend continuously in the range *ca.* 30° if the rotational disorder of the molecule was assumed. Because there are no nodes in such electron densities, no attempts to analytically divide into sites have been made in this disordered structure. These findings suggest a disorder structure of the 18-Crown-6 molecules. These peaks are clearly resolved and the disorder may be described in terms of two sites (containing Molecules of the same D_{3d} symmetry) rotated *ca.* 30° with respect to each other around the approximate three fold axis of rotation (see Figure 3). As a result, the coordinations of 18-Crown-6 ether atoms (O1-C6) were obtained by refinemint of the center of two site rotated *ca.* 30°.

The crystal packing of the anions and cations is shown in Figure 4. The hexamolybdocobaltate (III) anion is located on the (001) plane and sandwhiched in between two (18-

Crown-6.K)⁺ complexed cations. This sandwhich structure are aligned along the *a* axis. The anions connect with one after another through eight water molecules to a [OO1] direction (see Figure 2). All oxygen atoms in the anion coordinated to a water molecule or potassium ion. The stable packing arrangement is found in the crystal lattice.

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Crystal Structure of Bithionol, C₁₂H₆Cl₄O₂S

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The crystal structure of Bithionol, $C_{12}H_6Cl_4O_2S$, has been determined from X-ray intensity data measured by Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo-K$_\alpha$ radiation. The crystal data as follows; triclinic space group $P\bar{1}$, $a = 8.879(2)$, $b = 10.782(1)$, $c = 8.511(1)$Å, $\alpha = 115.43(1)$, $\beta = 115.22(1)$, $\gamma = 74.44\,°(1)$. $\mu = 9.51$ cm⁻, $F(000) = 356$, $Z = 2$. Final R value is 0.036 for independent 2669 observed reflections. Each six-membered benzene rings are coplanar within experimental errors and the dihedral angle between these planes is $81.28\,°(1)$. The S-(1) and S-C(7) distances are 1.787(2) and 1.791(3)Å, respectively.

Introduction

Bithionol and their different substituted derivatives are well known drugs and are particulary effective in human fascioliasis. Other flukicides of overall analogous structure contain -CONH and -CSNH bridges as well as bulky and different electron-withdrawing substituents. The geometrical configuration of the sulfur groups, X-S-Y and X-SO₂-Y, have been studied in several molecules. In the X-SO₂-Y, bond distribution about sulfur atom is found to depart significantly from that of a regular tetrahedron, with some dependence on substituent atoms X and Y. The sulfon group is of particular interest when linked to two aromatic rings, in view of the molecular orbital investigation of diphenyl sulfon by Koch & Moffitt[1]. These authors predicted overlap of 3*d* orbitals of sulfur atom with adjacent carbon atom 2*p* orbitals, resulting in an angle of 90° between the normals to the aromatic rings and common C-S-C plane.

Experimental

The title compound was provided by Dongkwang Chemicals Co.. Colorless rectangular crystals were grown from acetone solution. Weissenberg photographies showed them to be triclinic, space group P1̄, the crystal density was measured by floatation method in 2,3-dibromopro-pene/iso-propyl alcohol. A crystal of 0.4 × 0.4 × 0.41 mm was used for reflecton data collection with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. Unit cell parameters were determined from 25 reflections having $20 < 2\theta < 26°$. Intensities were measured for 2754 reflections with $\sin\theta/\lambda < 0.70$Å, indices in the range $-10 < h < 10, -14 < k < 12, 0 < l < 11$ using $\omega/2\theta$ scans with a scan width $\Delta\omega = (0.7 + 0.35 \tan\theta)°$ and scan rate 8.24 °/minute. Three monitor reflections ((3,6,2), (1,7,3), (4,4,0)) showed deviations less than 2% from their average intensities. No absorption corrections were applied. 2754 measured reflections of which 2669 with $|Fo| > 2\sigma(Fo)$ were used in structure determination and refinement. The crystal structure was solved by direct methods (SHELXS-86[2]) and refined by full-matrix least squares (SHELX-76[3]) with anisotropic temperature factor for non-hydrogen atoms and isotropic for hydrogen atoms. Atomic scattering factors for non-hydrogen atoms were taken from Cromer & Waber[4], and those for hydrogen atoms from Stewart, Davidson & Simpson[5]. Refinment minimized was $\Sigma w\Delta^2$, $\Delta = |Fo| - |Fc|$ and $w = 1/[\sigma^2(Fo) + 0.001 Fo^2]$. All hydrogen atoms were located in a difference Fourier map. Final positional parameters with e.s.d.s are Table 1. In the final cycle of refinement the largest parameter shift $(\Delta/\sigma)_{max}$ was 0.01. The agreement indices were R = 0.036 and R$_w$ = 0.037. Maximum residual electron density in final difference Fourier syn-