

Supplementary Material Available: Tables of observed and calculated structure factors (51 pages) for all five compounds. Ordering information is given on any current masthead page.

References and Notes

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- (4) For a list see: Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.*

- companion paper in this issue. See also: Cotton, F. A.; Rice, G. W.; Hanson, B. E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 953.
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A New Compound Containing the Tetrasulfatodimolybdenum Anion with a Bond Order of 3.5

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The $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ ion has been obtained in the form of a compound with the formula $\text{K}_4[\text{Mo}_2(\text{SO}_4)_4]\text{Cl}\cdot 4\text{H}_2\text{O}$. This compound has many advantages over the previously known $\text{K}_3[\text{Mo}_2(\text{SO}_4)_4]\cdot 3.5\text{H}_2\text{O}$ for the study of the electronic structure and spectroscopic properties of the $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ ion. It crystallizes in the tetragonal space group $P4/mnc$ with cell dimensions $a = 11.930$ (2) Å, $c = 7.930$ (1) Å, $V = 1128$ (1) Å³, and $Z = 2$. The $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ ions occupy special positions with $4/m$ (C_{4h}) symmetry, and the Mo-Mo axes are all precisely parallel to the crystallographic c axis. The Cl^- ions lie between $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ ions so as to form continuous, linear $\cdots\text{Mo}\cdots\text{Mo}\cdots\text{Cl}\cdots\text{Mo}\cdots\text{Mo}\cdots\text{Cl}\cdots$ chains with very long, 2.881 (1) Å, weak Mo to Cl interactions. The Mo-Mo distance, 2.167 (2) Å, is identical within experimental error with that found in $\text{K}_3[\text{Mo}_2(\text{SO}_4)_4]\cdot 3.5\text{H}_2\text{O}$.

Introduction

Several years ago the first example of a metal-to-metal bond of order 3.5 based on a $\sigma^2\pi^4\delta$ configuration¹ was discovered in the form of the $\text{Mo}_2(\text{SO}_4)_4^{3-}$ ion.² This ion was obtained in the compound $\text{K}_3[\text{Mo}_2(\text{SO}_4)_4]\cdot 3.5\text{H}_2\text{O}$ that arose by spontaneous aerial oxidation of $\text{Mo}_2(\text{SO}_4)_4^{4-}$. This lavender compound has since been studied electrochemically,^{2b} by EPR^{2b} and electronic absorption spectroscopy,³ photochemically,^{3a} by Raman spectroscopy,⁴ and theoretically.⁵ In view of its interesting photochemistry and its somewhat puzzling Raman and electronic absorption spectra, further study was considered worthwhile. The crystals of $\text{K}_3[\text{Mo}_2(\text{SO}_4)_4]\cdot 3.5\text{H}_2\text{O}$ are inherently disadvantageous in several respects. First, they contain two crystallographically independent molecules. Second, there are two different, nearly perpendicular orientations of the Mo-Mo axes in the unit cell.

To facilitate more complete and unambiguous characterization of the electronic and spectroscopic properties of the $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ ion, a more advantageous crystal form was desirable. We report here a new compound, $\text{K}_4[\text{Mo}_2(\text{SO}_4)_4]\text{Cl}\cdot 4\text{H}_2\text{O}$, which ideally fulfills our objective.

Experimental Section

Preparation of $\text{K}_4[\text{Mo}_2(\text{SO}_4)_4]\text{Cl}\cdot 4\text{H}_2\text{O}$. A solution of $\text{K}_4\text{Mo}_2\text{Cl}_8$ (0.1 g), prepared by a literature method,⁶ in 50 mL of 2 M H_2SO_4 and 0.3 M HCl was made under N_2 . Three milliliters of H_2O_2 (0.025 M) was added dropwise with frequent agitation between additions. The color of the solution turned from deep red to gray-blue. KCl (0.05 g) was then added, and the solution was stirred at 0 °C for 1/2 h. The blue precipitate was filtered, washed with acetone and ether, and dried under vacuum; yield 0.095 g.

Single crystals were obtained by a slow diffusion through a glass

frit of the solution containing the $\text{Mo}_2(\text{SO}_4)_4^{3-}$ species and a solution of 0.1 M KCl.

X-ray Crystallography. A crystal of dimensions $0.1 \times 0.1 \times 0.1$ mm was attached to the end of a glass fiber and mounted on a Syntex $P1$ four-circle diffractometer. $\text{Mo K}\alpha$ (λ 0.710730 Å) radiation, with a graphite crystal monochromator in the incident beam, was used.

Rotation photographs and ω -scans of several strong reflections indicated that the crystal was of satisfactory quality. Preliminary examination showed that the crystal belonged to the tetragonal system, space group $P4/mnc$. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range $25^\circ < 2\theta < 35^\circ$ giving $a = 11.930$ (2) Å, $c = 7.930$ (1) Å, and $V = 1128$ (1) Å³. With these dimensions and $Z = 2$ (for the formula $\text{K}_4\text{Mo}_2(\text{SO}_4)_4\text{Cl}\cdot 4\text{H}_2\text{O}$; mol wt 840.05) the density is calculated to be 2.47 g cm⁻³. The density determined by flotation in a mixture of bromoform and carbon tetrachloride was 2.50 ± 0.05 g cm⁻³.

Data were measured by θ - 2θ scans. A total of 496 reflections in the range $0^\circ < 2\theta \leq 50^\circ$ were collected of which 437 having $I > 3\sigma(I)$ were used to solve and refine the structure. General procedures for data collection have been described elsewhere.⁷ The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is 23.6 cm⁻¹; no absorption correction was applied.

The heavy-atom positions were obtained from a three-dimensional Patterson function. The structure was refined⁸ in space group $P4/mnc$ to convergence by use of anisotropic thermal parameters for all the nonhydrogen atoms.

The discrepancy indices

$$R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2} / \sum w|F_o|^2$$

had final values of $R_1 = 0.035$ and $R_2 = 0.053$ with an error in an observation of unit weight equal to 1.25. The final difference map showed no peaks of structural significance. A list of the observed

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Mo(1)	0.0000 (0)	0.0000 (0)	0.3634 (1)	1.29 (4)	=B ₁₁	0.80 (3)	0	0	0
K(1)	0.3332 (3)	0.1668 (0)	-0.2500 (0)	3.3 (1)	=B ₁₁	2.09 (7)	-0.19 (8)	-1.72 (9)	=B ₁₃
Cl(1)	0.0000 (0)	0.0000 (0)	0.0000 (0)	3.3 (2)	=B ₁₁	1.0 (1)	0	0	0
S(1)	0.2714 (2)	0.4086 (2)	0.0000 (0)	1.38 (7)	1.55 (7)	1.65 (7)	-0.13 (7)	0	0
O(1)	0.3477 (3)	0.4191 (3)	0.1517 (5)	1.8 (2)	2.3 (2)	1.6 (2)	-0.6 (1)	-0.2 (1)	0.1 (1)
Ow(1)	0.4792 (6)	0.2253 (7)	-0.5000 (0)	2.7 (3)	4.7 (4)	3.5 (3)	-0.4 (3)	0	0
O(2)	0.2228 (5)	0.2978 (5)	0.0000 (0)	2.2 (2)	2.2 (2)	2.8 (3)	-0.5 (2)	0	0
O(3)	0.1907 (6)	0.4976 (6)	0.0000 (0)	2.8 (3)	3.0 (3)	2.8 (3)	1.0 (2)	0	0

^a The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}k lb^*c^*)]$.

Table II. Bond Distances (Å) and Bond Angles (deg) for $K_4Mo_2(SO_4)_4Cl \cdot 4H_2O$

Distances			
Mo(1)-Mo(1)'	2.167 (2)	S(1)-O(1)	1.514 (4)
-Cl(1)	2.881 (1)	-O(2)	1.444 (6)
-O(1)	2.061 (4)	-O(3)	1.433 (6)
Angles			
Mo(1)-Mo(1)-O(1)	93.3 (1)	O(1)-S(1)-O(1)'''	105.2 (3)
O(1)-Mo(1)-O(1)'	173.3 (2)	-O(2)	108.5 (2)
-O(1)''	89.81 (1)	-O(3)	110.0 (2)
Mo(1)-O(1)-S(1)	121.5 (2)	O(2)-S(1)-O(3)	114.1 (3)

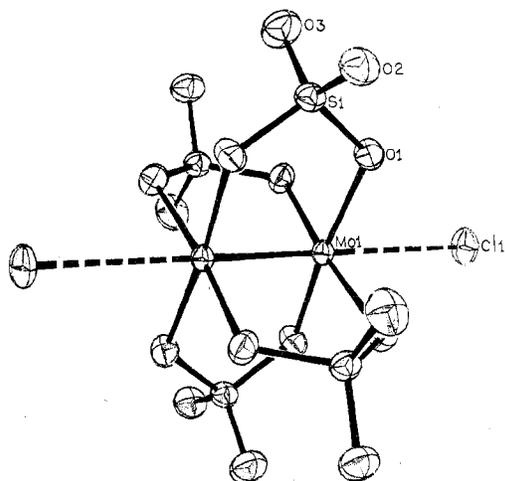


Figure 1. The Cl...[Mo₂(SO₄)₄]...Cl unit with each atom represented by its ellipsoid of thermal vibration, scaled to enclose 40% of its electron density. Each of the six crystallographically independent atoms is labeled; all others are related to these by the 4/m symmetry.

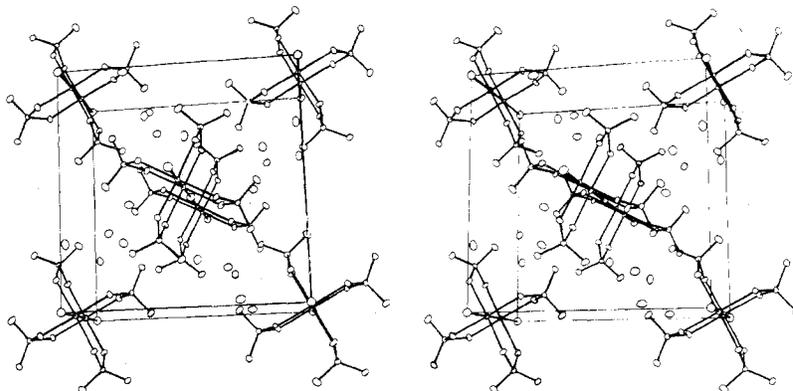


Figure 2. Stereoscopic view of one unit cell, looking nearly parallel to the *c* direction. In the center of the cell the symmetrical bridging by Cl⁻ ions is evident. Atoms unconnected by any bonds are water oxygen atoms and K⁺ ions.

and calculated structure factors is available as supplementary material.

Results and Discussion

The atomic positional and thermal parameters are listed in Table I. Figure 1 shows the Cl...[Mo₂(SO₄)₄]...Cl unit and defines the numbering scheme, while Figure 2 gives a stereoview of the contents of the entire unit cell. Interatomic distances and angles are listed in Table II. Every atom in the cell occupies some kind of special position except for the oxygen atoms, O(1), that are bound to molybdenum. The water molecules are not bound to molybdenum.

The [Mo₂(SO₄)₄]³⁻ ion as a whole is situated with its midpoint at 0, 0, 1/2, which is a special position of 4/m (*C*_{4h}) symmetry. The Mo-Mo bond lies precisely along the *c* axis of the unit cell. The Cl⁻ ions lie at the origin (and at each of the other seven vertices of the tetragonal cell). The structure therefore consists of infinite chains of ...Cl...[Mo₂(SO₄)₄]...Cl... parallel to the *z* direction along each of the *c* edges of the unit cell, and down the center. The K⁺ ions and water molecules are found in the interior of each cell.

The Mo...Cl distance, 2.881 (1) Å, indicates that there is only weak, if any, Mo-Cl bonding and that coupling between one [Mo₂(SO₄)₄]³⁻ ion and the next one through the intervening Cl⁻ ion should be slight. The [Mo₂(SO₄)₄]³⁻ ion itself has rigorous *C*_{4h} symmetry and comes very close to having *D*_{4h} symmetry. The deviations from the latter are seen in the different bond distances from sulfur to the exo oxygen atoms and in the difference between the O(1)-S-O(2) and O(1)-S-O(3) angles. Actually, the difference in the exo S-O distances is not, statistically speaking, real. The difference, 1.5°, between the angles, each of which has an esd of 0.2°, is almost certainly real, though small.

The dimensions found here for the [Mo₂(SO₄)₄]³⁻ unit are the same to within the uncertainties as those found² in the compound K₃[Mo₂(SO₄)₄]·3.5H₂O. The Mo-Mo distances

for the two molecules in this case were 2.167 (1) and 2.162 (1) Å, while that which we find here is 2.167 (2) Å. In the former, the average of the eight independent Mo–O distances (with the mean deviation) is 2.065 ± 0.010 Å, which may be compared to 2.061 (4) Å found here. Similarly, the S–O distances for coordinated oxygen atoms are 1.521 ± 0.003 Å formerly and 1.514 (4) Å in the present case, and those for the uncoordinated oxygen atoms are 1.442 ± 0.005 Å and 1.438 (6) Å, respectively.

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Registry No. $K_4[Mo_2(SO_4)_4]Cl \cdot 4H_2O$, 69429-51-2; $K_4Mo_2Cl_8$, 25448-39-9.

Supplementary Material Available: A table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

References and Notes

- (a) It should be remembered that a bond order of 3.5 also results from a $\sigma^2\pi^4\delta^2\delta^*$ configuration, the first example of this being the $Tc_2Cl_8^{3-}$ ion, whose structure,^{1b} bonding,^{1c} and electronic absorption spectrum^{1d} are well-known. (b) Cotton, F. A.; Shive, L. W. *Inorg. Chem.* **1975**, *14*, 2032. (c) Cotton, F. A.; Kalbacher, B. J. *Ibid.* **1977**, *16*, 2386. (d) Cotton, F. A.; Fanwick, P. E.; Gage, L. D.; Kalbacher, B. J.; Martin, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 5642.
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- All crystallographic computing was done on a PDP 11/45 computer at the Molecular Structure Corp., College Station, TX, with the Enraf-Nonius structure determination package.

Notes

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Structure of Thiotriithiazyl Tribromide ($S_4N_3^+$)(Br_3^-): A Low Molecular Weight Sulfur–Nitrogen Compound Containing a Trihalide Counterion

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The discovery of superconductivity in $(SN)_x$ ¹ and its brominated derivative $(SNBr_{0.4})_x$ ^{2,3} has fostered a resurgence of interest in the chemistry of small S–N compounds and their reactions with halogens. Our efforts in this area have been twofold: to synthesize and characterize low molecular weight analogues of $(SN)_x$ ^{4,5} and to unravel the complexities of the reaction of $(SN)_x$ precursors such as S_4N_4 with halogens. Recently it has been shown that the reaction of solid S_4N_4 with bromine vapor yields a brominated derivative of $(SN)_x$ ^{6,7} while reaction with liquid bromine yields the title compound, $(S_4N_3^+)(Br_3^-)$.⁸ $(S_4N_3^+)(Br_3^-)$ is an interesting material for several reasons. In addition to being one of the few stable compounds containing the tribromide ion, it may be of importance because of the potential understanding its structure may shed on the unknown structure of $(SNBr_{0.4})_x$. Since brominated $(SN)_x$ does not lend itself to single-crystal X-ray diffraction studies, the question of what the major Br species are and their relationship to the $(SN)_x$ lattice have been attacked by such indirect methods as EXAFS, IR, and the like. In all of these methods some type of standard is necessary. $(S_4N_3^+)(Br_3^-)$ is one such excellent standard.

Experimental Section

The compound was prepared as previously described,⁸ crystallizing in large clusters of fused single crystals. With considerable effort an irregularly shaped fragment of approximate dimensions $0.2 \times 0.2 \times 0.35$ mm suitable for X-ray diffraction was found and mounted

in a Lindemann glass capillary under an argon atmosphere. The crystal was transferred to an Enraf-Nonius CAD4 diffractometer where, subsequent to initial machine location and autoindexing of eight reflections, a preliminary unit cell and orientation matrix were computed. The least-squares refinement of the setting angles of 13 high-angle reflections ($2\theta \geq 30^\circ$, graphite-monochromatized Mo $K\alpha_1$ radiation, λ 0.709 30 Å) then yielded the monoclinic cell dimensions $a = 6.105$ (2) Å, $b = 8.792$ (2) Å, $c = 18.060$ (4) Å, and $\beta = 91.58$ (1)°. There are four formula units per cell.

Data were collected by the θ – 2θ scan method to $2\theta = 50^\circ$. The scan range was calculated according to $\Delta\theta = (0.70 + 0.35 \tan \theta)^\circ$ and was extended by 25% on each end for background measurement. The scan rate, based on a fast prescan, was computed such that 10⁴ counts were to be obtained, if possible, in a maximum time of 90 s. An aperture 4 mm high and $(3.5 + 0.87 \tan \theta)$ mm wide was placed in front of the counter 173 mm from the crystal. The intensities of 3 standard reflections, measured after every 50 reflections, remained constant over the course of data collection.

The data were reduced as described previously,^{9,10} with the value of ϵ in the expression for $\sigma(F_o^2)$ taken to be 0.04. An absorption correction ($\mu = 139.67$ cm⁻¹) was applied to the data, although the irregular shape of the crystal could only be grossly approximated. The values of the transmission coefficients ranged between 0.07 and 0.19. An analysis of the systematic absences ($0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$) indicated the space group to be $P2_1/c$ (C_{2h}^5 , No. 14).¹¹ The structure was solved by direct methods using MULTAN,¹² which revealed the positions of the Br atoms. Refinement and subsequent difference maps revealed the remaining atoms. Complete anisotropic refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged at $R = 0.065$ and $R_w = 0.074$, based on 91 variables and 1129 reflections for which $F_o^2 \geq 3\sigma(F_o^2)$. The weights were taken as $4F_o^2/\sigma^2(F_o^2)$. The error in an observation of unit weight was computed to be 2.48. In the last cycle no parameter changed by more than 0.002σ . The scattering factors were taken from ref 13. Corrections for the anomalous scattering¹⁴ of Br and S were applied to the calculated structure factors. Final atomic positional and thermal parameters are compiled in Table I.

Results and Discussion

The atom numbering scheme for the $S_4N_3^+$ ring is shown