The Synthesis and Crystal Structure of a Novel Dinuclear Molybdenum Compound with a Single Sulfur Bridge $[(CH_3)_4N]_2[Mo_2O_2S(S_2)_4]\cdot CH_3CN$

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Abstract

A novel dinuclear molybdenum compound with a single sulfur bridge is reported herein. It is the first example of a dinuclear molybdenum compound containing a $[Mo_2O_2S]$ structural complex. The title compound crystallizes in a monoclinic space group $P2_1/n$ with the following unit cell dimensions: $a = 9.281(2)$, $b = 14.712(6)$, $c = 18.699(7)$ Å, $\beta = 95.10(3)°$, $V = 2543$ Å^3, $Z = 4$, $D_c = 1.833$ g cm^{-3}. Diffraction data of 3810 reflections with $I \geqslant 3\sigma(I)$ have been collected on a CAD-4 four-circle diffractometer using Mo Kα radiation. The structure has been determined by Patterson and direct methods and refined by a least-squares method to a final R index of 0.053. The structure determination shows that the angle between the molybdenum atoms Mo–S–Mo is 91.59(4)°.

Introduction

An extensive chemistry of the synthesis and structure of molybdenum sulfur compounds has emerged in recent years. Many dinuclear molybdenum compounds containing a $[Mo_2O_2S_2]$ structural complex have been reported [1]. Hereinafter, we report the first example of a dinuclear molybdenum compound containing a $[Mo_2O_2S]$ structural complex with a single sulfur bridge, in addition to four disulfur chelating terminal ligands. Nowadays, people are paying more attention to the chemistry of disulfur molybdenum complexes, since it may lead to the elucidation of some interesting features in bioinorganic chemistry [2]. Indeed some new reactions with organic ligands have already been discovered [3].

Experimental

All reactants and organic solvents were obtained commercially of at least CP grade.

Synthesis of the Title Compound

A mixture of 8.0 g $NH_2OH\cdot HCl$ and 8.0 g $(NH_4)_6Mo_7O_{24}$ was dissolved in 120 ml of water to form a yellow suspension. Then a solution of 7.0 g K_2S in 20 ml of water was added. The colour of the resultant solution changed gradually from yellow to red. This solution was heated at 55 °C for *ca.* 5 min, cooled to room temperature, and then filtered. Then a $(CH_3)_4NBr$ solution (obtained by dissolving 5.0 g $(CH_3)_4NBr$ in 10 ml of water) was added to the mother liquor whereby a red precipitate formed which was then filtered and washed with CH_3OH (20 ml) three times. The precipitate was then redissolved in 40 ml of CH_3CN. After evaporating in air for several days, *ca.* 0.8 g of dark-red crystals was obtained.

Elemental Analysis

Found: Mo, 27.84; S, 41.50; C, 16.55; H, 3.72; N, 5.89. Calc.: Mo, 27.62; S, 41.12; C, 17.12 H, 3.59; N, 5.98%.

IR Spectrum

IR spectra were recorded with a Perkin-Elmer 577 spectrophotometer using KBr pellets. IR (cm^{-1}): 950, 920, ν(Mo=O); 530, ν(S–S); 450, ν(Mo–S–Mo); 360, 342, ν(Mo–S).

Crystal Data

4753 independent reflections were collected in a CAD-4 diffractometer with Mo Kα radiation in the range of $1° < \theta \leqslant 25°$. All reflections with $I \geqslant 3\sigma(I)$ were used for structure determination. Intensities were corrected for Lp factors and empirical absorption. The crystal is monoclinic belonging to the space group $P2_1/n$ with the following unit cell dimensions: $a = 9.281(2)$, $b = 14.712(6)$, $c = 18.699(7)$ Å, $\beta = 95.10(3)°$, $Z = 4$, $V = 2543$ Å^3, $D_c = 1.833$ g cm^{-3}.

Structure Determination

Computations were performed using SDP programs provided by Enraf-Nonius. The structure was solved by Patterson and Fourier methods. The

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coordinates of the two molybdenum atoms were determined; then the other remaining non-hydrogen atoms were located from successive difference Fourier synthesis. The structures were refined by full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms. The final R index is 0.053.

The atomic coordinates and thermal parameters are listed in Table I, and the important bond lengths and bond angles are given in Tables II and III, respectively. See also 'Supplementary Material'.

TABLE I. Positional Parameters (e.s.d.s in parentheses)

Atom	x	y	z	B (A^2)^a
Mo(1)	−0.22461(6)	0.13200(4)	−0.12851(3)	2.00(1)
Mo(2)	0.34385(6)	−0.35741(4)	0.10886(3)	1.67(1)
S	−0.2588(2)	0.2349(1)	−0.02707(9)	2.52(4)
S(1)	−0.1110(2)	0.2663(1)	−0.1706(1)	2.71(4)
S(2)	−0.1686(3)	0.1695(2)	−0.2470(1)	3.44(4)
S(3)	−0.3698(2)	0.0097(1)	−0.1825(1)	3.04(4)
S(4)	−0.4243(2)	0.0562(1)	−0.0845(1)	3.15(4)
S(5)	−0.4468(3)	0.3517(2)	−0.2294(1)	3.18(4)
S(6)	−0.4783(2)	0.2363(1)	−0.1711(1)	2.43(4)
S(7)	−0.2304(3)	0.4938(1)	−0.1453(1)	3.52(4)
S(8)	−0.1323(2)	0.4304(1)	−0.0559(1)	3.13(4)
O(1)	−0.0827(6)	0.0733(4)	−0.0906(3)	4.1(1)
O(2)	−0.4745(6)	0.3998(4)	−0.0606(3)	3.0(1)
N(1)	0.2398(6)	0.2230(4)	0.0303(3)	2.4(1)
C(1)	0.390(1)	0.2172(9)	0.0667(6)	5.6(3)
C(2)	0.129(1)	0.206(2)	0.0760(7)	12.4(6)
C(3)	0.218(2)	0.315(1)	0.011(1)	15.4(7)
C(4)	0.228(2)	0.176(1)	−0.0351(8)	15.7(5)
N(2)	0.2371(6)	0.5662(4)	−0.1688(3)	2.5(1)
C(5)	0.1080(9)	0.6227(5)	−0.1534(5)	3.5(2)
C(6)	0.362(1)	0.5877(7)	−0.1154(5)	4.2(2)
C(7)	0.276(1)	0.5854(7)	−0.2438(4)	4.3(2)
C(8)	0.199(1)	0.4660(6)	−0.1632(5)	4.4(2)
N(3)	−0.827(1)	0.3218(6)	−0.3218(5)	6.0(2)
C(9)	−0.770(1)	0.3731(6)	−0.3553(5)	4.1(2)
C(10)	−0.697(1)	0.4397(7)	−0.3962(5)	4.8(2)

^{a}Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2)$.

TABLE II. Bond Distances (A)

Atom 1–Atom 2	Distance
Mo(1)–S	2.469(1)
Mo(1)–S(1)	2.405(10
Mo(1)–S(2)	2.385(1)
Mo(1)–S(3)	2.415(1)
Mo(1)–S(4)	2.372(1)
Mo(1)–O(1)	1.677(4)
Mo(2)–S	2.449(1)
Mo(2)–S(5)	2.370(1)
Mo(2)–S(6)	2.415(1)
Mo(2)–S(7)	2.393(1)
Mo(2)–S(8)	2.375(1)
Mo(2)–O(2)	1.693(3)
S(1)–S(2)	2.053(2)
S(3)–S(4)	2.061(2)
S(5)–S(6)	2.053(2)
S(7)–S(8)	2.055(2)
N(1)–C(1)	1.502(7)
N(1)–C(2)	1.413(8)
N(1)–C(3)	1.419(11)
N(1)–C(4)	1.399(10)
N(2)–C(5)	1.506(6)
N(2)–C(6)	1 493(7)
N(2)–C(7)	1.506(7)
N(2)–C(8)	1.522(7)
N(3)–C(9)	1.144(8)
C(9)–C(10)	1 446(10)

TABLE III Bond Angles (°)

Atom 1–Atom 2–Atom 3	Angle
S–Mo(1)–S(1)	80.68(4)
S–Mo(1)–S(2)	128.70(5)
S–Mo(1)–S(3)	132.28(5)
S–Mo(1)–S(4)	82 16(5)
S–Mo(1)–O(1)	98.1(2)
S(1)–Mo(1)–S(2)	50.76(5)
S(1)–Mo(1)–S(3)	136.06(5)
S(1)–Mo(1)–S(4)	151.48(5)
S(1)–Mo(1)–O(1)	102.1(2)
S(2)–Mo(1)–S(3)	86.79(5)
S(2)–Mo(1)–S(4)	132.29(6)
S(2)–Mo(1)–O(1)	106.5(2)
S(3)–Mo(1)–S(4)	50.99(5)
S(3)–Mo(1)–O(1)	100.4(1)
S(4)–Mo(1)–O(1)	102.7(2)
S(6)–Mo(1)–O(1)	171.2(2)
S–Mo(2)–S(5)	130.39(5)
S–Mo(2)–S(6)	83 21(4)
S–Mo(2)–S(7)	132.04(5)
S–Mo(2)–S(8)	82.19(5)
S–Mo(2)–O(2)	98.3(1)
S(1)–Mo(2)–O(2)	170.5(1)
S(5)–Mo(2)–S(6)	50.80(5)
S(5)–Mo(2)–S(7)	84.80(5)
S(5)–Mo(2)–S(8)	131 36(5)
S(5)–Mo(2)–O(2)	105.8(1)
S(6)–Mo(2)–S(7)	134.70(5)
S(6)–Mo(2)–S(8)	155.14(5)
S(6)–Mo(2)–O(2)	99.5(1)
S(7)–Mo(2)–S(8)	51.05(5)
S(7)–Mo(2)–O(2)	101.4(1)
S(8)–Mo(2)–O(2)	102.5(1)
Mo(1)–S–Mo(2)	91.59(4)
Mo(1)–S(1)–S(2)	64.09(5)
Mo(1)–S(2)–S(1)	65.14(5)

(continued)

TABLE III. *(continued)*

Atom 1–Atom 2–Atom 3	Angle
Mo(1)–S(3)–S(4)	63.44(5)
Mo(1)–S(4)–S(3)	65.57(5)
Mo(2)–S(5)–S(6)	65.71(5)
Mo(2)–S(6)–S(5)	63.48(5)
Mo(2)–S(7)–S(8)	64.03(5)
Mo(2)–S(8)–S(7)	64.93(6)
C(1)–N(1)–C(2)	114.4(6)
C(1)–N(1)–C(3)	106.0(7)
C(1)–N(1)–C(4)	111.4(7)
C(2)–N(1)–C(3)	103.3(9)
C(2)–N(1)–C(4)	116.1(9)
C(3)–N(1)–C(4)	104.0(1)
C(5)–N(2)–C(6)	109.7(4)
C(5)–N(2)–C(7)	109.7(4)
C(5)–N(2)–C(8)	109.2(4)
C(6)–N(2)–C(7)	110.3(4)
C(6)–N(2)–C(8)	109.2(5)
C(7)–N(2)–C(8)	108.8(5)
N(3)–C(9)–C(10)	178.4(7)

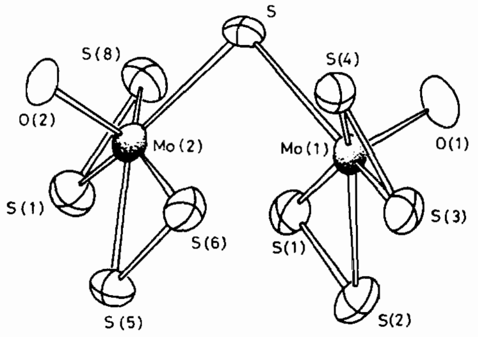

Fig. 1. The configuration of the anion $[Mo_2O_2S(S_2)_4]^{2-}$.

Results and Discussion

The structure consists of the cation $[(CH_3)_4N]^+$ and the anion $[Mo_2O_2S(S_2)_4]^{2-}$, together with a solvent molecule CH_3CN. A perspective view of the anion is given in Fig. 1. The lone sulfur atom is bonded to two molybdenum atoms to form a sulfur bridge. The angle Mo–S–Mo is 91.59(4)°. The Mo–S bond length is 2.46 Å. This bond distance corresponds to a Mo–S single bond. There is no metal–metal bond between the Mo atoms in the anion. Several compounds containing a $[Mo_2O_3]$ structure unit with a single oxygen bridge have been reported [1]. However compounds containing a $[Mo_2O_2S]$ structural complex with single sulfur bridges have not yet been reported, although Müller and Christophlienk [4] succeeded in the synthesis of a dinuclear molybdenum anion $[Mo_2S(CN)_{12}]^{4-}$ with such a single sulfur bridge, but without any Mo=O bond. In the anion $[Mo_2S(CN)_{12}]^{4-}$, the angle Mo–S–Mo is 169.5(2)° and the Mo–S bond length is 2.173 Å. It is essentially a linear bridge adjoining a pair of Mo=S double bonds. Obviously, the anion $[Mo_2O_2S(S_2)_4]^{2-}$ must differ from the $[Mo_2S(CN)_{12}]^{4-}$ to a great extent. In addition, the local octahedral coordination around each of the Mo atoms is formed from two disulfur ligands, together with one sulfur atom and one oxygen atom.

It is interesting to note that his novel compound reacts with CuCl and PPh_3 and forms rather easily the cubane-like cluster $[Cu_3MoS_3Cl](PPh_3)_3O$ which Müller *et al.* [5] succeeded in synthesising in a different way.

Supplementary Material

Observed and calculated structure factors are available from the Editor-in-Chief.

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References

1 E. I. Stiefel, *Prog. Inorg. Chem., 22,* 1 (1975).
2 A. Müller, W. Jaegermann and J. H. Enemark, *Coord. Chem. Rev., 46,* 5476 (1982).
3 T. R. Halbert, W.-H. Pan and E. I. Stiefel, *J. Am. Chem. Soc., 105,* 245 (1983).
4 A. Müller and P. Christophliemk, *Angew. Chem., Int. Ed. Engl., 8,* 753 (1969).
5 A. Müller, H. Bögge, H. G. Tolle, R. Jostes, U. Schimanski and M. Dartmann, *Angew. Chem., Int. Ed. Engl., 19,* 654 (1980).