X-Ray Structure of μ-Oxo-μ-sulfido-bis[(cysteinato)oxomolybdate(V)] Complex, $Ca[Mo_2O_3S(SCH_2CH(NH_2)CO_2)_2]\cdot 3H_2O$

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(Received December 15,1986)

Synopsis. The crystal structure of μ-oxo-μ-sulfido cysteinato Mo(V) dimer, $Ca[Mo_2O_3S(SCH_2CH(NH_2)CO_2)_2]\cdot 3H_2O$ has been determined from X-ray diffraction data. The structure of the complex anion is similar to those of di-μ-oxo- and di-μ-sulfido- Mo(V) dimers. The trans influence of sulfur atoms is observed.

As model compounds of some enzymes,[1] many molybdenum(V) complexes with di-μ-oxo, μ-oxo-μ-sulfido, or di-μ-sulfido bridges have been prepared and characterized. Cysteine (or its derivatives) is one of the ligands most frequently used in these investigations; Raman and resonance Raman spectra[2] and pulse-radiolysis study[3] on the cysteinato complexes have been reported and the X-ray structures of di-μ-oxo-[4] and di-μ-sulfido-bis[(cysteinato)oxomolybdate(V)][5] complexes have also been revealed. However, the X-ray structure of μ-oxo-μ-sulfido-bis [(cysteinato)oxomolybdate(V)], has not yet been determined. In view of the importance of this complex, we have carried out the X-ray crystal structure analysis of the title compound and we report here the result obtained.

Experimental

Preparation of Calcium μ-Oxo-μ-sulfido-bis[(cysteinato) oxomolybdate(V)] Trihydrate, $Ca[Mo_2O_3S(cys)_2]\cdot 3H_2O$. Corresponding sodium salt[6] (1 g) was dissolved in 10 mL of water and filtered. Solid $CaCl_2\cdot 2H_2O$ (ca. 1 g) was added to the filtrate. Cooling of the filtrate in a refrigerator gave red crystals (ca. 0.7 g). Anal. Found: N, 4.39; C, 11.54; H, 2.76%. Calcd for $C_6H_{12}O_{10}N_2S_3CaMo_2$: N, 4.66; C, 12.00; H, 2.01%.

X-Ray Data Collection. Crystal data: F. W.=600.3, orthorhombic, space group $P2_12_12_1$, a=16.430 (2), b=10.557 (2), c=9.782(2) Å, Z=4, D_c=2.35 g cm^{-3}, μ(Mo $K\alpha$)=21.4 cm^{-1}, λ(Mo $K\alpha$)=0.7107 Å, V=1696.7 (4) Å^3. The intensities were measured on a Philips PW1100 diffractometer. Crystal size: 0.20×0.26×0.45 mm^3; scan speed, 0.033° s^{-1}; scan range, 1.2°; back ground measurement at each side of the scan range, half of the scan time; maximam 2θ value, 50°; number of reflections ($F_o^2 \geqq 2\sigma(F_o^2)$), 2150. No correction was made for absorption. The refinement of the structure was performed by the block diagonal least-squares method. The function minimized was $w(|F_d|-|F_d|)^2$, where $w=1/\sigma^2(F_o)$ was used. The final R value was 0.026, $R_w=[\Sigma w\Delta F^2/\Sigma wF_o^2]^{1/2}$= 0.036. In the final cycles of the refinement hydrogen atoms were included but their parameters were not refined. All the hydrogen atoms except for those bound to the water oxygens were located at the calculated positions. All the parameter shifts were less than 0.3σ. The maximum peak in the final difference synthesis was 1.0 e Å^{-3}. The atomic scattering factors, with corrections for anormalous scattering of Mo and S, were taken from Ref. 7. The F_o—F_c tables, anisotropic thermal parameters, and coordinates of the hydrogen atoms are preserved by the Chemical Society of Japan (Document No. 8744). The atomic coordinates are listed in Table 1. Computations were performed on a FACOM 230-60 computer at Osaka City University and on a ACOS 900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. The figure was drawn by the use of ORTEP.[8] The programs in the UNICS[9] were employed.

Results and Discussion

Recrystallization of the sodium salt gives only a

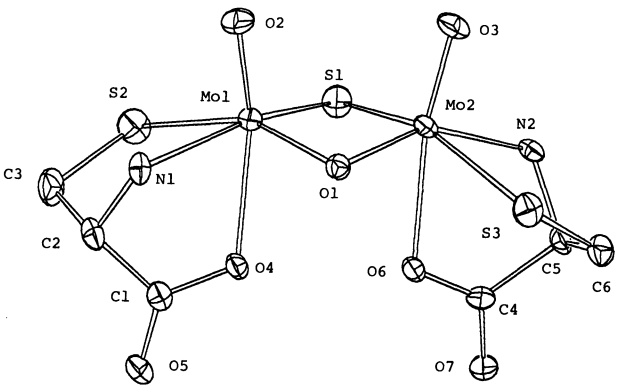

Fig. 1. Perspective view of $[Mo_2O_3S(cys)_2]^{2-}$.

Table 1. Fractional Coordinates and Temperature Factors[10] with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Mo1	0.28734(2)	0.19550(4)	0.78538(4)	1.16	C5	0.4683(3)	0.4694(5)	1.1267(5)	1.4
Mo2	0.36778(3)	0.24974(4)	1.02107(4)	1.20	C6	0.5325(3)	0.3759(6)	1.1652(5)	1.9
Ca	0.4853(1)	0.7435(1)	0.7402(1)	1.40	O1	0.3973(2)	0.1484(3)	0.8608(3)	1.3
S1	0.2563(1)	0.3618(1)	0.9312(1)	1.80	O2	0.2325(2)	0.0698(4)	0.8396(4)	2.2
S2	0.1939(1)	0.3026(1)	0.6309(1)	2.11	O3	0.3214(3)	0.1524(4)	1.1341(4)	2.3
S3	0.5123(1)	0.2192(1)	1.0871(1)	1.90	O4	0.3813(2)	0.3040(3)	0.6545(3)	1.3
N1	0.3127(3)	0.0961(4)	0.5865(4)	1.5	O5	0.4052(3)	0.3688(4)	0.4425(4)	2.5
N2	0.3874(3)	0.4133(4)	1.1571(4)	1.4	O6	0.4401(2)	0.4082(3)	0.8996(3)	1.3
C1	0.3720(3)	0.2964(5)	0.5246(5)	1.4	O7	0.5037(2)	0.5938(4)	0.9286(4)	1.9
C2	0.3144(3)	0.1936(5)	0.4774(5)	1.6	WA1	0.3604(3)	0.8375(4)	0.6451(5)	2.6
C3	0.2284(4)	0.2466(6)	0.4637(5)	2.2	WA2	0.3919(3)	0.5764(4)	0.6874(5)	2.8
C4	0.4715(3)	0.4953(4)	0.9736(5)	1.3	WA3	0.4496(3)	0.9008(4)	0.9052(4)	2.2

Table 2. Interatomic Distances and Bond Angles with Estimated Standard Deviation in Parentheses

Bond distance	l/Å	Bond distance	l/Å	Bond distance	l/Å	Bond distance	l/Å
Mo1-S1	2.319(1)	Mo1-O2	1.689(4)	Mo2-O3	1.692(4)	C4-C5	1.523(7)
Mo1-S2	2.433(1)	Mo1-O4	2.310(3)	N1-C2	1.483(6)	C4-O6	1.278(6)
Mo1-N1	2.249(4)	Mo2-O1	1.959(3)	N2-C5	1.485(7)	C4-O7	1.247(6)
Mo2-S1	2.351(1)	Mo2-O3	1.692(4)	C1-C2	1.512(7)	C5-C6	1.493(8)
Mo2-S3	2.482(1)	Mo2-O6	2.372(3)	C1-O4	1.282(6)		
Mo2-N2	2.203(4)	Mo1-Mo2	2.718(1)	C1-O5	1.236(7)		
Mo1-O1	2.013(3)	Mo1-O2	1.689(4)	C2-C3	1.526(8)		

Short contact[a)]	l/Å	Short contact[a)]	l/Å	Short contact[a)]	l/Å	Short contact[a)]	l/Å
N2-O5^{I}	2.876(6)	Ca-O4^{II}	2.504(4)	WA1-N1^{III}	2.897(6)	WA3-O1^{III}	2.786(5)
Ca-O1^{II}	2.389(4)	Ca-O6^{II}	2.528(4)	WA1-O3^{IV}	2.990(6)	WA3-O5^{II}	2.832(6)

Bond angle	ϕ/°	Bond angle	ϕ/°	Bond angle	ϕ/°	Bond angle	ϕ/°
S1-Mo1-S2	83.77(5)	O1-Mo1-O2	99.7(2)	N2-Mo2-O1	151.0(2)	N1-C2-C1	106.9(4)
S1-Mo1-N1	157.8(1)	O1-Mo1-O4	74.1(1)	N2-Mo2-O3	98.5(2)	N1-C2-C3	107.5(4)
S1-Mo1-O1	99.1(1)	O2-Mo1-O4	156.9(2)	N2-Mo2-O6	71.1(1)	C1-C2-C3	110.1(5)
S1-Mo1-O2	106.5(1)	S1-Mo2-S3	155.22(5)	O1-Mo2-O3	107.6(2)	C5-C4-O6	114.5(4)
S1-Mo1-O4	96.4(1)	S1-Mo2-N2	86.9(1)	O1-Mo2-O6	82.0(1)	C5-C4-O7	120.7(4)
S2-Mo1-N1	78.2(1)	S1-Mo2-O1	99.7(1)	O3-Mo2-O6	169.2(2)	O6-C4-O7	124.8(5)
S2-Mo1-O1	155.3(1)	S1-Mo2-O3	101.5(2)	Mo1-S1-Mo2	71.20(4)	N2-C5-C4	107.4(4)
S2-Mo1-O2	103.0(1)	S1-Mo2-O6	81.2(1)	Mo1-N1-C2	107.6(3)	N2-C5-C6	108.5(4)
S2-Mo1-O4	81.2(1)	S3-Mo2-N2	78.7(1)	Mo2-N2-C5	108.8(3)	C4-C5-C6	110.0(4)
N1-Mo1-O1	92.0(1)	S3-Mo2-O1	84.3(1)	C2-C1-O4	115.0(4)	Mo1-O1-Mo2	86.4(1)
N1-Mo1-O2	90.2(2)	S3-Mo2-O3	100.5(2)	C2-C1-O5	121.5(4)	Mo1-O4-C1	116.0(3)
N1-Mo1-O4	68.2(1)	S3-Mo2-O6	75.1(1)	O4-C1-O5	123.5(5)	Mo2-O6-C4	115.2(3)

a) Roman numeral superscripts refer to atoms in the positions:
I x, y, 1+z; II 1−x, 1/2+y, 3/2−z; III x, 1+y, z; IV 1/2−x, 1−y, −1/2+z

Table 3. Comparison of the Bond Distances (l/Å) and Angles (ϕ/°)

	2[a)]	1[b)]	3[c)]		2[a)]	1[b)]	3[c)]
Mo-Mo	2.569(2)	2.718(1)	2.82(0.3)	Mo-O$_{cysteine}$	2.295(16)	2.310(3)	2.38(2.5)
Mo-O$_{bridge}$	1.946(15)[d)]	2.013(3)[d)]			2.295)14)	2.372(3)	2.35(2.5)
	1.954(15)[d)]	1.959(3)[e)]		Mo-N	2.260(16)	2.249(4)[f)]	2.31(2.5)
	1.907(15)[e)]				2.200(17)	2.203(4)[g)]	2.22(2.5)
	1.915(15)[e)]			Mo-S$_{cyseine}$	2.490(6)	2.482(1)[f)]	2.51(0.9)
Mo-O$_{terminal}$	1.706(18)	1.689(4)	1.69(2.5)		2.491(6)	2.433(1)[g)]	2.48(0.9)
	1.712(16)	1.692(4)	1.55(2.5)	Mo-O-Mo	83.6(6)	86.4(1)	
Mo-S$_{bridge}$		2.351(1)[d)]	2.34(0.9)[d)]		83.2(6)		
		2.319(1)[e)]	2.37(0.9)[d)]	Mo-S-Mo		71.20(4)	75
			2.32(0.9)[e)]				75
			2.30(0.9)[e)]	D[h)]	151	157.8(4)	155.6

a) Ref. 4. b) This work. c) Ref. 5. d) Trans to S$_{cysteine}$. e) Trans to N. f) Trans to S$_{bridge}$. g) Trans to O$_{bridge}$. h) Dihedral angle between the two MoS_2, MoOS, or MoO_2 planes.

powdery product. Addition of solid KCl or NH_4Cl to the aqueous solution of the sodium salt provides no precipitate, while that of $CaCl_2 \cdot 2H_2O$, $BaCl_2 \cdot 2H_2O$, or $MgCl_2 \cdot 6H_2O$ gives crystals of respective salts, of which calcium salt is best for the X-ray analysis. Perspective view of the complex anion, $[Mo_2O_3S(cys)_2]^{2-}$ (**1**), is shown in Fig. 1. The structure of the anion is similar to those of the di-μ-oxo- ($[Mo_2O_2(cys)_2]^{2-}$, (**2**)) and di-μ-sulfido ($[Mo_2O_2S_2(cys)_2]^{2-}$, (**3**)) complexes. Interatomic distances and bond angles are listed in Table 2. Comparison of dimensions is made in Table 3. The Mo-Mo distance and dihedral angle of the μ-oxo-μ-sulfido complex is closer to the respective values of the di-μ-sulfido complex than to those of the di-μ-oxo complex. The Mo-O-Mo angle of **2** is larger than the corresponding angles of **1**, while the Mo-S-Mo angle of **2** is smaller than those of **3**. The trans influence of sulfur atoms (S$_{bridge}$ and S$_{cysteine}$) is observed in **1**, as is observed in **2** and **3**: Mo-N, Mo-O, and Mo-S bonds trans to the sulfur atom (S$_{bridge}$ or S$_{cysteine}$) are longer than those trans to ligating N or O atom, respectively.

We are grateful to Mr. Motoji Akiyama for the help of the preparative work.

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