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The Preparation and X-Ray Structures of Di-μ-sulfido- and μ-Oxo-μ-sulfido-bis[tris(isothiocyanato)oxomolybdate(V)] Ions

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The crystal structures of $(pyH)_4[Mo_2O_2S_2(NCS)_6]$ (**1**) (pyH=pyridinium ion) and $(pyH)_4[Mo_2O_3S(NCS)_6]\cdot 2H_2O$ (**2**) have been determined from the diffractometer data. The **1** and **2** structures were refined by the least-squares method to R 0.041 and 0.064 for 2728 and 2349 non-zero reflections respectively. The two structures are isomorphous. Each Mo(V) ion has a distorted octahedral coordination, and two coordination octahedra share a common edge to form a binuclear complex. The binuclear complex contains a mirror plane through two bridging atoms. The two terminal oxo ligands on each Mo(V) are *cis* to each other and *cis* to the bridging oxo or sulfido. The Mo–N(NCS) bond length *trans* to the Mo–O_t (terminal oxo) is *ca.* 0.1 Å longer than the other Mo–N(NCS) bond lengths, showing the large *trans* effect of the O_t ligand.

Although the preparation and X-ray structure of the $(pyH)_4[Mo_2O_4(NCS)_6]\cdot H_2O$ complex with the di-μ-oxo bridge have been reported,1) no similar complex containing the di-μ-sulfido or μ-oxo-μ-sulfido bridge has yet been prepared. In this paper, we wish to describe the preparation and structures of $(pyH)_4[Mo_2O_2S_2(NCS)_6]$ (**1**) and $(pyH)_4[Mo_2O_3S(NCS)_6]\cdot 2H_2O$ (**2**) and to compare the structures of the two complexes with that of $(pyH)_4[Mo_2O_4(NCS)_6]\cdot H_2O$1) in connection with the *trans* bond-weekening effects of the terminal oxo, bridging oxo, and bridging sulfido.

Experimental

Preparation of 1 and 2. Complex **1** was prepared by the addition of sodium thiocyanate about six times the molar quantity of the aqua-ion $[Mo_2O_2S_2(H_2O)_6]^{2+}$ in 1 mol dm^{-3} of HCl,2) followed by the drop-by-drop addition of pyridine (*ca.* one thirtieth of the volume of the aqua-ion solution). After the solution had stood in a refrigerator a couple of days, the red crystals which had deposited were filtered by suction and air-dried. Yield, 85%. Found: N, 14.67; C, 32.51; H, 2.53%. Calcd for $(pyH)_4[Mo_2O_2S_2(NCS)_6]$: N, 14.64; C, 32.64; H, 2.53%.

Complex **2** was prepared similarly by the use of the aqua ion $[Mo_2O_3S(H_2O)_6]^{2+}$ in 1 mol dm^{-3} HCl3) instead of the $[Mo_2O_2S_2(H_2O)_6]^{2+}$ used for the preparation of **1**. Yield, 70%. Found: N, 14.87; C, 33.29; H, 2.50%. Calcd for $(pyH)_4[Mo_2O_3S(NCS)_6]\cdot 2H_2O$: N, 14.34; C, 31.97; H, 2.89%.

X-Ray-data Collection. Complex **1** crystallizes in the form of red square-prisms. The crystal of **2** is thin red plate. The **1** and **2** crystals were mounted in an arbitrary orientation on a Philips PW1100 automated diffractometer. The PW1100 programs obtained 17 centered reflections for **1** and 15 for **2**, and an orientation matrix for each crystal, and then identified the monoclinic cells for the two crystals. The $P2_1/m$ space group for **1** and **2** was assumed throughout the structure analyses and was confirmed by the successful refinement of the structures. The unit-cell dimensions were refined by the least-squares analyses of the θ values of 36 reflections for **1** and of 38 for **2**. The crystal data and experimental details for **1** and **2** are given in Table 1. The intensity data were collected by the use of Mo *Ka* radiation. During the data collection, three standard reflections were monitored every 4 h to check the stability and orientation of each crystal. Both compounds remained quite stable. Each data set was corrected for Lorenz-polarization effects,4) but *not* for absorption.

Structure Solution and Refinement. The structure of **1** was first solved by the Patterson-Fourier method. The structure solution of **2** was straightforward because the **1** and **2** structures are isomorphous. The refinement of the structures was carried out by the use of the block-diagonal least-squares method. The function minimized was $\sum w(F_o-|F_c|)^2$, where $w=1/\sigma^2(F_o)$ was used. The neutral atomic scattering factors for the Mo, S, O, N, and C atoms were taken from Ref. 5, with an anomalous dispersion corrections ($\Delta f'$) for the Mo and S atoms. The final R values were 0.041 for **1** and 0.064 for **2**. No attempt was made to locate hydrogen atoms. The N atom of the pyridinium ion could not be identified in either crystal. The positions of the N atoms were detemined on the basis of short contact distances (Table 4), because the N–H group of the pyridinium ion is expected to form a hydrogen bond. No chemically significant peaks were observed on the final difference Fourier maps for **1** and **2**. The maximum peaks were 0.6 e Å^{-3} for **1** and 0.6 e Å^{-3} for **2**. No water of crystallization was found in **1**. The F_o-F_c tables for **1** and **2** and the anisotropic temperature factors are preserved by the Chemical Society of Japan (Document No. 8340). The final atomic coordinates are given in Tables 2 and 3. The figures were drawn by the use of ORTEP.6) The computations were performed by the use of a FACOM 230-60 computer at Osaka City University and an ACOS-900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University, using Programs in the UNICS.7)

Results and Discussion

Perspective views of the complex ions in **1** and **2** are given in Figs. 1 and 2. Each complex contains a crystallographic mirror plane through the two bridging atoms. Therefore, both complexes have the *cis*-dioxo structure. Each structure consists of two distorted octahedra sharing as SS or OS edge. The geometries and dimensions of $Mo_2O_2S_2$ and Mo_2O_3S cores do not significantly differ from those of the corresponding cores in the other binuclear Mo(V) complexes. The deviation of the Mo atom from the mean plane defined by the S_2N_2 plane to O1 is 0.28 Å in **1**, while that from the OSN_2 plane to O1 is 0.28 Å in **2**. The bond distances and angles are listed in Table 4, while important interatomic distances and dihedral angles are compared in Table 5. The Mo–Mo and O1–O1 distances are larger in **1** than in **2**, in

TABLE 1. SUMMARY OF CRYSTAL DATA AND EXPERIMENTAL DETAILS

Compound	**1** $(pyH)_4[Mo_2O_2S_2(NCS)_6]$	**2** $(pyH)_4[Mo_2O_3S(NCS)_6]\cdot 2H_2O$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$
a/Å	15.669 (5)	15.898 (9)
b/Å	13.107 (4)	13.207 (4)
c/Å	9.173 (3)	9.085 (4)
β/°	96.77 (3)	94.04 (4)
$F(000)$	996	980
F.W.	993.0	976.9
U/Å^3	1870.8 (10)	1902.7 (15)
Z	2	2
D_m/g cm^{-3}	1.74	1.68
D_c/g cm^{-3}	1.76	1.70
μ(Mo $K\alpha$)/cm^{-1}	11.4	10.7
Crystal size/mm^3	0.08×0.08×0.13	0.04×0.08×0.14
Scan type	ω	ω
Scan speed/° s^{-1}	0.033	0.033
Scan range/°	0.9	1.0
$2\theta_{max}$/°	50	50
Background measurement	Half of the scan time	Half of the scan time
Number of unique reflections with $F_o^2 \geqq 3\sigma(F_o^2)$	2728	2349
$R(R')$	0.041 (0.060)	0.064 (0.085)

TABLE 2. ATOMIC COORDINATES (× 10^5 FOR Mo AND × 10^4 FOR OTHERS) AND TEMPERATURE FACTORS (× 10^4 FOR Mo AND × 10^3 FOR OTHERS) FOR **1** $(pyH)_4[Mo_2O_2S_2(NCS)_6]$, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	U_{eq}/Å^2 [a)]
Mo	18082 (3)	35785 (5)	3970 (5)	427
S1	3411 (2)	5890 (2)	3932 (3)	92
S2	848 (2)	5915 (3)	−3625 (3)	112
S3	4557 (2)	4035 (2)	−1945 (2)	70
S4	1319 (2)	2500	−1516 (2)	44
S5	2643 (2)	2500	1948 (2)	48
O1	929 (3)	3747 (4)	1260 (5)	58
N1	2457 (4)	4788 (5)	1724 (6)	63
N2	1400 (4)	4796 (5)	−1154 (6)	63
N3	3003 (4)	3851 (5)	−725 (6)	57
C1	2852 (4)	5229 (5)	2668 (7)	53
C2	1166 (4)	5247 (5)	−2192 (7)	55
C3	3636 (4)	3943 (5)	−1240 (6)	49
NA1	1108 (6)	2500	4380 (9)	96
CA2	1479 (6)	1603 (6)	4714 (8)	75
CA3	2299 (6)	1603 (6)	5479 (7)	81
CA4	2710 (7)	2500	5846 (10)	68
NB1	9335 (7)	2500	9750 (11)	146
CB2	9242 (7)	1614 (8)	9021 (13)	130
CB3	8959 (7)	1657 (9)	7402 (13)	129
CB4	8863 (9)	2500	6836 (15)	111
NC1	4732 (5)	2500	1428 (10)	72
CC2	4741 (4)	1609 (5)	2167 (8)	60
CC3	4756 (5)	1592 (6)	3617 (9)	68
CC4	4771 (6)	2500	4402 (11)	70
ND1	7000 (7)	2500	2766 (13)	103
CD2	6952 (6)	1593 (6)	2026 (11)	88
CD3	6860 (6)	1584 (8)	520 (9)	96
CD4	6774 (8)	2500	−236 (12)	114

a) $U_{eq} = (U_{11}+U_{22}+U_{33})/3$.

TABLE 3. ATOMIC COORDINATES (× 10^5 FOR Mo AND × 10^4 FOR OTHERS) AND TEMPERATURE FACTORS (× 10^4 FOR Mo AND × 10^3 FOR OTHERS) FOR **2** $(pyH)_4[Mo_2O_3S(NCS)_6]\cdot 2H_2O$, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	v	z	U_{eq}/Å^2 [a)]
Mo	17567 (6)	35176 (7)	2266 (8)	480
S1	3264 (3)	5870 (4)	3701 (5)	120
S2	837 (4)	5843 (5)	−3682 (6)	157
S3	4492 (2)	4074 (3)	−2173 (5)	90
S4	1294 (3)	2500	−1732 (4)	51
O2	2391 (6)	2500	1397 (9)	54
O1	895 (5)	3687 (6)	1145 (7)	63
N1	2416 (6)	4630 (7)	1644 (10)	69
N2	1422 (6)	4766 (7)	−1246 (9)	66
N3	2984 (6)	3752 (7)	−863 (9)	63
C1	2771 (7)	5156 (9)	2487 (12)	67
C2	1196 (7)	5241 (9)	−2217 (11)	62
C3	3605 (7)	3890 (8)	−1373 (10)	57
NA1	1165 (10)	2500	4271 (14)	103
CA2	1562 (10)	1609 (10)	4586 (12)	93
CA3	2386 (10)	1625 (11)	5241 (12)	98
CA4	2794 (13)	2500	5558 (17)	90
NB1	9319 (10)	2500	9760 (15)	153
CB2	9238 (10)	1592 (13)	9007 (19)	133
CB3	9010 (10)	1594 (13)	7589 (18)	123
CB4	8826 (14)	2500	6943 (23)	126
NC1	3994 (11)	2500	2236 (17)	93
CC2	4301 (10)	1702 (12)	2634 (16)	117
CC3	4968 (10)	1599 (9)	3701 (17)	104
CC4	5313 (15)	2500	4220 (23)	113
ND1	5962 (11)	2500	−201 (18)	107
CD2	6275 (11)	1600 (12)	285 (22)	131
CD3	6933 (10)	1619 (13)	1384 (27)	150
CD4	7252 (15)	2500	1858 (34)	142
OW	9026 (8)	1291 (10)	3301 (13)	146

a) $U_{eq} = (U_{11}+U_{22}+U_{33})/3$.

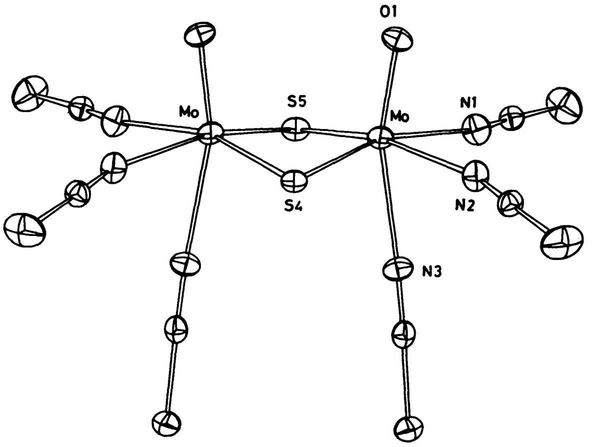

Fig. 1. A perspective view of $[Mo_2O_2S_2(NCS)_6]^{4-}$. The thermal ellipsoid was drawn at the 40% probability level.

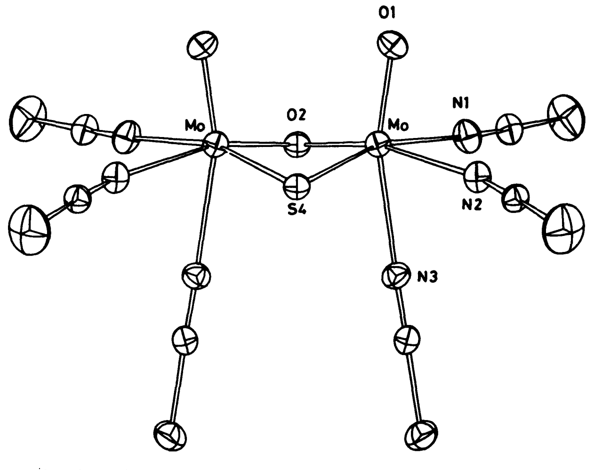

Fig. 2. A perspective view of $[Mo_2O_3S(NCS)_6]^{4-}$.

accordance with the larger size of the sulfur compared to that of the oxygen in the bridge. On the other hand, the S_b–Mo–O1 (S_b: bridging sulfido) and O_b–Mo–O1 (O_b : bridging oxo) angles in the cores in **1** and **2** have similar values. The angle between the two MoS_2 planes in **1** is very close to that between the two MoOS planes in **2**. The MoS_2–MoS_2 dihedral angle of 153.4° and the MoOS–MoOS dihedral angle of 153.8° are similar to those in $Ba[Mo_2O_4(ox)_2(H_2O)_2]\cdot 10H_2O$[8] and $Cs_2[Mo_2O_2S_2(ox)_2(H_2O)_2]\cdot 2H_2O$,[9] but smaller than those in $K_6[\{Mo_2O_3S(ox)_2\}_2(ox)]\cdot 10H_2O$[3] and $K_6[\{Mo_2O_4(mal)_2\}_2(mal)]\cdot 4H_2O$.[10] The Mo–O1 distance in **1** is 1.683 Å and that in **2**, 1.669 Å. These values are in agreement with those previously reported.[11] The Mo–S (bridging sulfido) distances in **1** and **2** range from 2.301 to 2.313 Å, and the Mo–O (bridging oxo) distance in **2** is 1.950 Å. The S–Mo–S, O–Mo–S, Mo–S–Mo, and Mo–O–Mo angles in the bridges agree well with those in $Na_2[Mo_2S_2O_2(R\text{-}pdta)]\cdot 4H_2O$,[12] and $Na_2[Mo_2O_3S(R\text{-}pdta)]\cdot 4H_2O$.[12] The bond lengths and angles for the $Mo_2S_2O_2$ core in **1** are similar to those in $Na_2[Mo_2O_2S_2(R\text{-}pdta)]\cdot 4H_2O$, and the bond lengths and angles for the Mo_2O_3S core in **2** are similar to those in $Na_2[Mo_2O_3S(R\text{-}pdta)]\cdot 4H_2O$. The large trans effect of terminal oxo (O_t=O1) was observed in these cases,

TABLE 4. INTERATOMIC DISTANCES AND ANGLES, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond length	l/Å		Bond angle	ϕ/°	
	1	**2**		**1**	**2**
Mo–O1	1.683(6)	1.669(6)	S4–Mo–S5	101.95(8)	
Mo–S4	2.313(2)	2.308(4)	S4–Mo–O2		98.3(3)
Mo–S5	2.301(2)		Mo–S4–Mo	75.36(7)	71.2(2)
Mo–O2		1.950(9)	Mo–S5–Mo	75.81(7)	
Mo–N1	2.176(6)	2.17(2)	Mo–O2–Mo		87.1(4)
Mo–N2	2.183(6)	2.17(3)	S5–Mo–O1	103.1(2)	
Mo–N3	2.269(6)	2.27(2)	S4–Mo–O1	102.8(2)	103.6(3)
N1–C1	1.16(1)	1.15(3)	O2–Mo–O1		103.4(4)
N2–C2	1.14(1)	1.12(4)	N1–Mo–O1	89.7(3)	89.5(5)
N3–C3	1.15(1)	1.13(2)	N2–Mo–O1	91.0(3)	91.8(7)
C1–S1	1.620(7)	1.61(3)	N3–Mo–O1	163.4(3)	163.9(5)
C2–S2	1.609(7)	1.62(4)	Mo–N1–C1	162.8(6)	174(2)
C3–S3	1.655(7)	1.65(3)	Mo–N2–C2	163.9(6)	164(3)
Mo–Mo	2.827(2)	2.688(2)	Mo–N3–C3	175.7(6)	178(1)
O1···O1	3.269(9)	3.14(2)	N1–C1–S1	177.2(7)	178(2)
N3···N3	3.54(2)	3.31(4)	N2–C2–S2	178.0(7)	175(3)
Short contact			N3–C3–S3	177.9(6)	178(2)
NA1···S2(I)[a)]	3.699(9)				
NA1···O1(II)	3.28(1)	3.25(2)			
NB1···O1(III)	3.16(2)	3.14(2)			
NC1···S5(II)	3.363(9)				
NC1···O2(II)		2.61(2)			
ND1···S3(II)		3.52(2)			

a) Roman numerals refer to the following equivalent positions: (I) $-x, -1/2+y, -z$; (II) $x, 1/2-y, z$; (III) $1+x, 1/2-y, 1+z$.

Table 5. Comparison of the interatomic distances[a] and dihedral angles

	l/Å								ϕ/°
	Mo–O$_t$	Mo–O$_b$	Mo–S$_b$	Mo–N[b]	Mo–N[c]	Mo–N[d]	Mo–Mo	O$_t$···O$_t$	D[e]
1	1.683 (6)		2.301 (2) 2.313 (2)	2.269 (6)	2.176 (6) 2.183 (6)		2.827 (2)	3.269 (9)	153.4
2	1.669 (6)	1.950 (9)	2.308 (4)	2.27 (2)	2.17 (2)	2.17 (3)	2.688 (2)	3.14 (2)	153.8
3[f]	1.645 (5)	1.954 (3)		2.251 (7)		2.142 (4)	2.581 (1)		

a) O$_t$: Terminal oxo; O$_b$: bridging oxo; S$_b$: bridging sulfido, b) *trans* to O$_t$, c) *trans* to S$_b$, d) *trans* to O$_b$, e) Dihedral angle between the two MoS$_2$ or MoOS planes. f) Average values except for the Mo–Mo distance in (pyH)$_4$[Mo$_2$O$_4$(NCS)$_6$]·H$_2$O; Ref. 1.

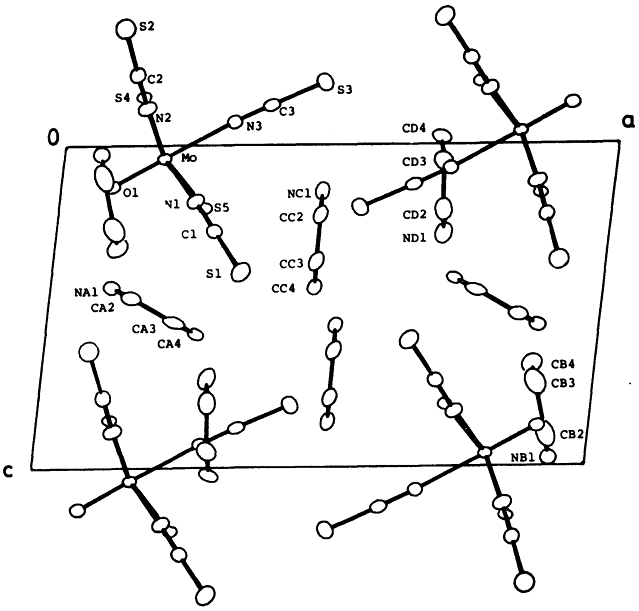

Fig. 3. Crystal structure of (pyH)$_4$[Mo$_2$O$_2$S$_2$(NCS)$_6$] viewed down the b axis.

too. The Mo–N bonds trans to O$_t$(O1) are *ca.* 0.1 Å longer than the other Mo–N bonds, as in the case of (pyH)$_4$[Mo$_2$O$_4$(NCS)$_6$]·H$_2$O.[1] We found no significant difference between the Mo–N bond lengths *trans* to the bridging oxo and those trans to the bridging sulfido.

The crystal structure of **1**, as viewed down the b axis, is shown in Fig. 3. The crystal consists of [Mo$_2$O$_2$S$_2$(NCS)$_6$]$^{4-}$ ions, and (pyH)$^+$ ions. The short contact distances are given in Table 4.

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