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The Preparation of Pyridinium μ-Oxo-bis[nitrilotriacetatodioxomolybdate(VI)] and Pyridinium Di-μ-oxo-bis[nitrilotriacetatooxomolybdate(V)] Monohydrate and the X-ray Structure of the Molybdenum(VI) Complex

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Synopsis. Nitrilotriacetato complexes of Mo^{VI} and Mo^{V} were prepared and the X-ray structure of the former complex is described. On the basis of the UV-visible and IR spectra and elemental analyses, the latter complex is formulated as $(pyH)_2[Mo_2O_4(ntaH)_2]\cdot H_2O$.

As a part of studies on the structure of molybdenum complexes,[1–3] we describe here the preparation of nitrilotriacetato complexes of Mo^{VI} and Mo^{V}, and the X-ray structure of the molybdenum(VI) complex.

Experimental

Preparation of $(pyH)_2[Mo_2O_5(ntaH)_2]$ (1). Pyridine(py) was added to nitrilotriacetic acid(ntaH$_3$) (2 m mol) in 20 ml of water and the solution was adjusted to pH 7—8. To this solution was added 2 m mol of MoO_3 and the suspension was warmed on a water bath with stirring for 0.5 h at 60 °C. During the reaction pyridine was added in order to keep pH 7—8. The resulting solution was filtered, evaporated to 4 ml, and methanol (5 ml) and acetone (8 ml) added. Colorless crystals were obtained after standing a couple of days. Yield, 270 mg. Found: C, 32.50; H, 3.36; N, 6.87%. Calcd for $(pyH)_2[Mo_2O_5(ntaH)_2]$; C, 32.60; H, 3.24; N, 6.92%.

Preparation of $(pyH)_2[Mo_2O_4(ntaH)_2]\cdot H_2O$ (2). $(pyH)_2[MoOCl_5]$ (2 m mol) and ntaH$_3$ (2 m mol) were added to 20 ml of water. The solution was warmed at 60 °C with stirring for 0.5 h and was adjusted to pH 7—8 with pyridine. The solution was filtered, evaporated to 7 ml, and methanol (5 ml) and acetone (5 ml) were added. Brown crystals were obtained after standing for 24 h. Yield, 520 mg. Found: C, 32.47; H, 3.58; N, 6.83%. Calcd for $(pyH)_2[Mo_2O_4(ntaH)_2]\cdot H_2O$: C, 32.52; H, 3.48; N, 6.90%.

Crystal Data of 1: $C_{22}H_{26}O_{17}N_4Mo_2$, F. W.=810.4, triclinic, space group $P\bar{1}$, $a=17.244(8)$ Å, $b=12.161(4)$ Å, $c=7.558(2)$ Å, $\alpha=104.99(3)°$, $\beta=83.36(3)°$, $\gamma=74.88(3)°$, $Z=2$, $D_m=1.84\ g\ cm^{-3}$, $D_c=1.86\ g\ cm^{-3}$, $\mu(Mo\ K\alpha)=9.42\ cm^{-1}$, $\lambda(Mo\ K\alpha)=0.7107$ Å, $U=1449.3(8)$ Å^3.

The intensities were measured on a Philips PW1100 diffractometer. Crystal size: 0.23×0.32×0.39 mm^3; scan speed: 0.033° s^{-1}; scan range: 1.0°; backgroung measurement at each side of the scan range: half of the scan time; maximum 2θ value: 50°; number of reflections with $F_o^2 \geqq 3\sigma(F_o^2)$: 4338.

The refinement of the structure was performed by 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 R value was 0.031 ($R_w=[\sum w\Delta F^2/\sum wF_o^2]^{1/2}=0.047$). In the final cycles of the refinement hydrogen atoms were included but their parameters were not refined. Hydrogen atoms defined by the geometry of the complex were located at calculated positions and those bonded to OA5 and OB5 atoms were found in the difference Fourier map. All the parameter shifts were less than 0.3σ. The maximum peak in the final difference Fourier map was 0.6 eÅ^{-3}. The atomic scattering factors, with corrections for anomalous scattering of Mo were taken from Ref. 4. The F_o-F_c Tables, anisotropic temperature factors, and coordinates of hydrogen atoms are preserved by the Chemical Society of Japan (Document No. 8429). The atomic coordinates are listed in Table 1. Computations were performed on a FACOM 230-60 computer at Osaka City University and on an ACOS 900 computer at the Crystallographic Research Center. Institute for Protein Research, Osaka University. The programs in the UNICS were used.[5]

The absorption spectrum was recorded on a Hitachi 330 spectrophotometer and infrared spectra were obtained in KBr disks with a JASCO IRA-1 spectrophotometer.

Results and Discussion

Figure 1 gives a perspective view of the complex in **1**. The complex has an approximate two fold axis. The complex consists of two octahedra sharing a single non-linear oxo bridge (MoA-OB-MoB=167.0(2)°). The two terminal oxo ligands on each Mo are mutually cis and cis to the bridging oxo. The $Mo(O_t)_2$ (O_t=terminal oxo) groups lie on the same side of the complex. The distorted octahedral coordination of each Mo is formed by two terminal and one bridging oxo (O_b), and two carboxylato oxygen atoms and one amino nitrogen atom of ntaH. One carboxylate group in ntaH is free from the coordination. The Mo–O_t distances (1.683(3)—1.700(3) Å) are comparable to those in cis dioxo complexes (Table 2).[6] The average Mo–O_b distance is 1.876(6) Å. The two Mo–O distances to the ntaH ligand in each Mo at 2.072(2) (trans to O_b) and 2.151(6) Å (trans to O_t) indicate that O_t has a larger trans bond weakening effect. The Mo–N bond (trans to O_t) is longer than

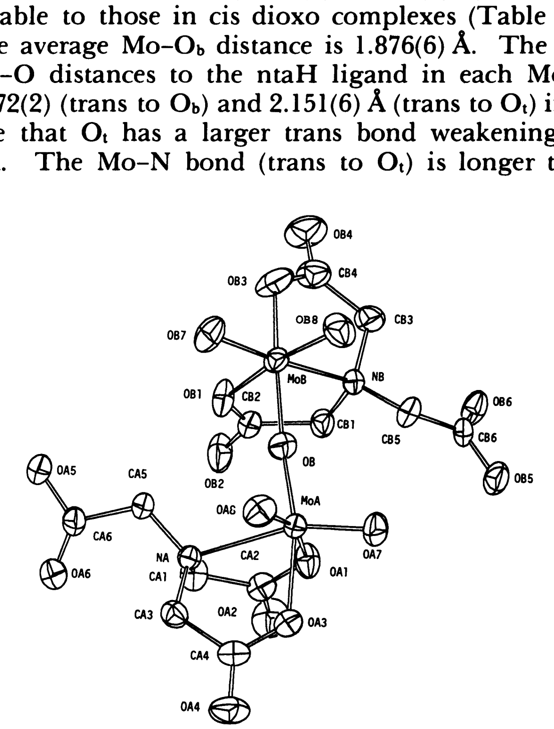

Fig. 1. A perspective view of $[Mo_2O_5(ntaH)_2]^{2-}$.

Table 1. Atomic coordinates and temperature factors for $(pyH)_2[Mo_2O_5(ntaH)_2]$ with their estimated standard deviations in parentheses

Atom	x	y	z	$U_{eq}/\text{Å}^2$ [a]
MoA	0.15255(2)	0.14765(3)	0.27443(5)	0.0282
NA	0.2809(2)	0.1925(3)	0.2724(4)	0.028
OA1	0.1769(2)	0.1962(3)	0.0249(4)	0.045
OA2	0.2424(2)	0.2854(3)	−0.1333(5)	0.064
OA3	0.1245(2)	0.3315(3)	0.3773(4)	0.039
OA4	0.1566(2)	0.4916(3)	0.5219(5)	0.052
OA5	0.4847(2)	0.0136(3)	0.2843(5)	0.051
OA6	0.4395(2)	0.2092(3)	0.3293(5)	0.055
OA7	0.0535(2)	0.1628(3)	0.2559(5)	0.049
OA8	0.1607(2)	0.1304(3)	0.4876(4)	0.045
CA1	0.3058(3)	0.2108(4)	0.0898(6)	0.039
CA2	0.2371(3)	0.2356(4)	−0.0146(5)	0.033
CA3	0.2608(3)	0.3045(4)	0.4286(6)	0.035
CA4	0.1754(3)	0.3840(3)	0.4447(5)	0.034
CA5	0.3441(3)	0.0938(4)	0.3021(6)	0.039
CA6	0.4276(3)	0.1132(4)	0.3062(6)	0.037
OB	0.2101(2)	−0.0080(2)	0.1252(4)	0.041
MoB	0.74578(2)	0.17435(3)	−0.01603(5)	0.0289
NB	0.7966(2)	0.1441(3)	0.2594(4)	0.028
OB1	0.6568(2)	0.1219(3)	0.1407(4)	0.046
OB2	0.6241(2)	0.0358(3)	0.3516(5)	0.056
OB3	0.6896(2)	0.3313(3)	0.2001(4)	0.048
OB4	0.6657(3)	0.4391(3)	0.4944(5)	0.055
OB5	0.9948(2)	−0.0506(3)	0.2614(4)	0.042
OB6	0.9097(2)	0.0968(3)	0.5021(4)	0.042
OB7	0.6828(2)	0.2200(3)	−0.1573(4)	0.049
OB8	0.8289(2)	0.2174(3)	−0.0644(5)	0.055
CB1	0.7503(3)	0.0764(4)	0.3395(6)	0.038
CB2	0.6708(2)	0.0787(4)	0.2745(5)	0.032
CB3	0.7813(3)	0.2654(4)	0.3901(6)	0.040
CB4	0.7063(3)	0.3526(4)	0.3690(6)	0.043
CB5	0.8847(3)	0.0762(4)	0.1926(6)	0.036
CB6	0.9307(2)	0.0418(4)	0.3378(6)	0.033
NC	−0.0206(3)	0.6729(4)	0.0289(6)	0.062
CC1	0.0474(3)	0.6120(5)	−0.0954(7)	0.057
CC2	0.1146(3)	0.5577(4)	−0.0426(8)	0.058
CC3	0.1133(3)	0.5679(5)	0.1429(8)	0.066
CC4	0.0420(4)	0.6329(5)	0.2698(7)	0.070
CC5	−0.0232(4)	0.6843(5)	0.2084(8)	0.058
ND	0.5988(3)	0.5329(4)	0.1277(8)	0.087
CD1	0.5555(5)	0.6302(6)	0.2660(9)	0.096
CD2	0.5043(3)	0.7168(5)	0.0440(8)	0.059
CD3	0.5052(4)	0.7275(5)	0.2187(9)	0.080
CD4	0.5485(4)	0.6107(5)	−0.0969(8)	0.079
CD5	0.5975(4)	0.5210(5)	−0.0494(9)	0.069

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

Table 2. Interatomic distances and bond angles with their estimated standard deviations in parentheses

Bond length(l/Å)		Bond angle(ϕ/°)	
MoA-OB	1.870(3)	MoA-OB-MoB	167.0(2)
MoA-OA1	2.145(3)	OB-MoA-OA7	104.7(2)
MoA-OA3	2.071(3)	OB-MoA-OA8	99.2(2)
MoA-OA7	1.695(3)	OA7-MoA-OA8	106.4(2)
MoA-OA8	1.695(3)	OA1-MoA-NA	73.6(1)
MoA-NA	2.413(3)	OA3-MoA-NA	73.0(1)
MoB-OB	1.881(3)	OB-MoB-OB7	104.8(2)
MoB-OB1	2.156(3)	OB-MoB-OB8	100.3(2)
MoB-OB3	2.075(4)	OB7-MoB-OB8	105.3(2)
MoB-OB7	1.700(3)	OB1-MoB-NB	72.6(1)
MoB-OB8	1.683(3)	OB3-MoB-NB	73.4(1)
MoB-NB	2.426(3)		
Possible hydrogen bond(l/Å) [a]			
NC(I)···OA1	2.883(6)		
ND···OB3	2.766(7)		
OA5···OB2	2.581(5)		
OB5···OB6(II)	2.634(4)		

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

the Mo–O bond (trans to O_t).

The IR spectrum of **2** gives the stretching vibrations of the Mo=O groups at 920 and 945 cm^{-1} and that of the Mo_2O_2 group at 783 cm^{-1}.[7] The IR spectra of the symmetric and assymmetric stretching vibrations of the carboxylato groups are similar in **1** and **2**. The UV-visible spectrum of **2** in pH 4 sodium acetate/acetic acid buffer solution gives two absorption peaks at 380 nm (shoulder, $\varepsilon=162\ \mathrm{l\,mol^{-1}cm^{-1}}$) and 297 nm ($\varepsilon=5080\ \mathrm{l\,mol^{-1}\,cm^{-1}}$). The spectrum is similar to that of $[Mo_2O_4(edta)]^{2-}$.[8] On the basis of the UV-visible and IR spectra and elemental analyses we formulate **2** as pyridinium di-μ-oxo-bis[nitrilotriacetatooxomolybdate(V)] monohydrate, $(pyH)_2[Mo_2O_4(ntaH)_2]\cdot H_2O$.

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