

Crystal Structure and EPR Spectra of *cis*-Dioxo-molybdenum(V) Complex with *o*-Aminophenol

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The paramagnetic *cis*-dioxo-molybdenum(V) complex, $[\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3]_3[\text{Mo}^{\text{V}}\text{O}_2(\text{HNC}_6\text{H}_4\text{O})_2]$ was obtained by the reaction of tetra-butyl ammonium β -octamolybdate with *o*-aminophenol and ethylenediamine in the mixed solvent of CH_3OH and CH_3CN , and characterized by IR, NMR, EPR spectroscopy and X-ray diffraction analysis. The determination of single crystal X-ray analysis revealed that the central Mo^{V} ion metal center exhibits distorted octahedral coordination with *cis*-dioxo *o*-aminophenol. The EPR spectra of both the complex and flavoenzyme show similarly. Thus it suggests that the complex anion $[\text{Mo}^{\text{V}}\text{O}_2(\text{HNC}_6\text{H}_4\text{O})_2]^{3-}$ and flavoenzyme have related structure feature.

Keywords *cis*-dioxo-molybdenum(V) complex anion, *o*-aminophenol, oxomolybdoenzyme, X-ray crystallography, EPR spectra

Introduction

Molybdenum is widely used in biological systems due to the two basic forms: nitrogenases and oxotransferases or oxomolybdoenzymes. The latter as the mononuclear active sites of a much more diverse group of enzymes in general function catalytically transfer an oxygen atom either to or from a physiological acceptor/donor molecule.¹⁻³ Though numerous oxomolybdenum complexes with a range of ligands containing O and S atoms as donors have been stud-

ied extensively and highly significant advances have been made recently in defining structure and developing structure-function relationships of the oxomolybdoenzymes,^{4,9} the complete stereochemistry is still remained unsolved. The complexes containing N atoms as coordination donor atoms are rarely reported also. As most of the known Mo^{V} compounds are EPR active due to their d^1 electronic configuration, EPR spectroscopy has become one of the most powerful technique for study of Mo^{V} chemistry especially in the case of coordination feature of molybdenum complexes. Herein we describe the synthesis of one type of *cis*-dioxo-molybdenum(V) complex with *o*-aminophenol, the crystal structure, and make a comparison between the EPR spectra exhibited by the title complex and flavoenzyme.

Experimental

Materials

All reagents used were received from commercial supplies. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 1600 Series FT IR spectrometer. ¹H NMR spectra were recorded on a Bruker AM-500 spectrometer using CD_3COCD_3 as solvent. EPR spectra were measured with a Bruker-300 EPR spectrometer.

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Synthesis of $(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_3[\text{Mo}^{\text{V}}\text{O}_2(\text{HNC}_6\text{H}_4\text{O})_2]$

To a solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ prejusted to pH = 3.5 with chloric acid, $(n\text{-Bu})_4\text{NBr}$ was added and stirred for 1 h, a white precipitate of *tetra-n*-butyl ammonium β -octamolybdate produced, then it was filtered and dried in the air.

A mixture of *o*-aminophenol and *tetra-n*-butyl ammonium β -octamolybdate produced above in appropriated volume of solution of CH_3OH and CH_3CN was stirred for 6 h and filtered, and the filtrate was layered with Et_2O for 15 d and red crystals were obtained. Though the procedure of the synthesis of the title complex is not very complicated, obtaining crystals is very difficult because the crystals are air sensitive and unstable in the filtrate layered with Et_2O .

Crystal structure determination

X-ray diffraction data of the molybdenum complex were collected for the title complex on a Enraf-Nonius CAD4 diffractometer at (299 ± 1) K using graphite monochromated Mo $K\alpha$ radiation. An empirical absorption correction using the program DIFABS was applied. The structure was solved by heavy-atom Patterson methods. Non-hydrogen atoms were refined anisotropically while hydrogen atoms were included but not refined. All calculations were performed on F using SHELXTL PLUS (VMS). Crystal data and experimental details are listed in Table 1.

Results and discussion

The structure of $[\text{Mo}^{\text{V}}\text{O}_2(\text{HNC}_6\text{H}_4\text{O})_2]^{3+}$ is shown in Fig. 1 and the packing diagram is presented in Fig. 2. The atomic coordinates and thermal parameters are listed in Table 2, while bond lengths and bond angles are tabulated in Tables 3 and 4, respectively.

As illustrated by Fig. 1, the structure of the mononuclear anionic unit $[\text{Mo}^{\text{V}}\text{O}_2(\text{HNC}_6\text{H}_4\text{O})_2]^{3-}$ displays the *cis*-dioxo fashion with pseudo-octahedral $[\text{MoO}_6]$ coordination geometry. The terminal Mo—O distances are within the range of 0.1702(6)—0.1709(5) nm commonly encountered for structures with the *cis*- $[\text{MoO}_2]$ unit. The average Mo—N and Mo—O distances are 0.2012(6) nm and 0.2149(6) nm, respectively. The 2 + 2 + 2 pattern of Mo—O(N) distances is evident in the bonding param-

eters for the complex anion.

Table 1 Crystal data for $(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_3[\text{Mo}^{\text{V}}\text{O}_2(\text{HNC}_6\text{H}_4\text{O})_2]$

Formula weight	518.53
Temperature	(299 ± 1) K
Radiation(Mo $K\alpha$)	0.071073 nm
Crystal system	orthorhombic
Space group	<i>Pbca</i>
Unit cell dimitions	$a = 1.4086(3)$ nm $b = 1.3563(3)$ nm $c = 2.6372(5)$ nm
Volume	$5.038(3)$ nm ³
<i>Z</i>	4
Density (calculated)	1.367 g/cm ³
Absorption coefficient	54.00 cm ⁻¹
<i>F</i> (000)	2192.00
Crystal size	0.30 mm × 0.30 mm × 0.40 mm
$2\theta_{\text{max}}$	50°
Index ranges	$0 \leq h \leq 16$, $0 \leq k \leq 16$, $0 \leq l \leq 30$
Reflection collected	4956
Independent reflections	3697
Data/restraints/parameters	1976/0/289
Goodness-of-fit on F^2	0.98
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R = 0.057$, $wR = 0.058$
Largest diff. Peak and hole	670 and -890 e/nm ³

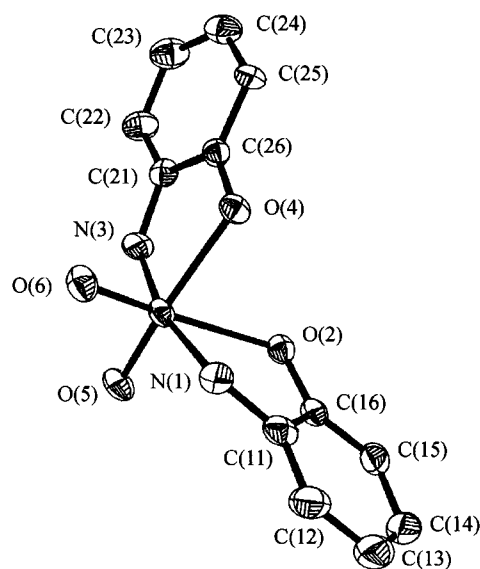


Fig. 1 Structure of $[\text{Mo}^{\text{V}}\text{O}_2(\text{HNC}_6\text{H}_4\text{O})_2]^{3-}$.

Since $[\text{MoO}_2(\text{HNC}_6\text{H}_4\text{O})_2]^{3-}$ is a trivalent anion, three ethylenediamine molecules must be presented as the

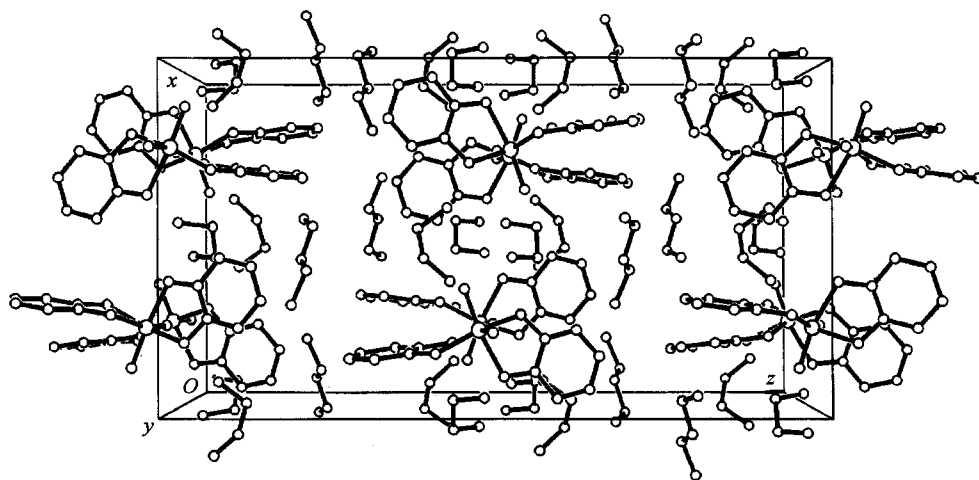


Fig. 2 Packing diagram of the title complex.

Table 2 Non-hydrogen atomic coordinates and thermal parameters

Atom	x	y	z	U_{eq}
Mo(1)	0.2499(1)	0.750(1)	0.4756(1)	0.035(1)
N(1)	0.1872(4)	0.1242(5)	0.4116(2)	0.044(1)
O(2)	0.2092(4)	-0.0572(4)	0.4346(2)	0.040(1)
C(11)	0.1842(5)	0.0604(7)	0.3726(3)	0.045(1)
C(12)	0.1703(7)	0.0911(9)	0.3222(4)	0.063(1)
C(13)	0.1679(8)	0.0021(1)	0.2839(4)	0.070(1)
C(14)	0.1781(8)	-0.0077(1)	0.2961(4)	0.076(1)
C(15)	0.1927(7)	-0.1122(8)	0.3474(4)	0.056(1)
C(16)	0.1952(5)	-0.0384(7)	0.3846(3)	0.039(1)
N(3)	0.2893(4)	0.0033(5)	0.5387(2)	0.047(1)
O(4)	0.1198(4)	0.0404(5)	0.5127(2)	0.041(1)
C(21)	0.2219(5)	-0.0163(6)	0.5750(3)	0.040(1)
C(22)	0.2450(9)	-0.0509(7)	0.6227(3)	0.056(1)
C(23)	0.1702(8)	-0.0672(9)	0.6572(4)	0.066(1)
C(24)	0.772(7)	-0.0509(7)	0.5421(4)	0.056(1)
C(25)	0.544(6)	-0.0139(7)	0.5933(3)	0.043(1)
C(26)	0.1302(6)	0.0042(6)	0.5598(3)	0.038(1)
O(5)	0.3627(4)	0.0579(5)	0.4542(3)	0.049(1)
O(6)	0.2482(6)	0.1941(4)	0.4966(2)	0.051(1)
C(31)	0.4553(5)	0.1628(5)	-0.0176(3)	0.029(1)
C(32)	0.4663(6)	0.2220(7)	-0.0662(3)	0.043(1)
C(33)	0.5557(6)	0.2801(7)	-0.0667(3)	0.045(1)
C(34)	0.5531(5)	0.3584(5)	-0.0266(3)	0.033(1)
C(41)	0.4121(5)	0.2808(7)	0.0748(3)	0.042(1)
C(42)	0.4718(9)	0.0303(1)	0.1193(5)	0.094(1)
C(43)	0.5562(8)	0.03609(9)	0.1097(4)	0.069(1)
C(44)	0.6211(5)	0.03206(6)	0.0698(3)	0.032(1)

Continued

Atom	x	y	z	U_{eq}
C(50)	-0.0190(1)	0.0804(1)	0.3118(9)	0.071(1)
C(51)	-0.0092(1)	0.0787(1)	0.2895(7)	0.127(1)
C(52)	-0.0613(9)	0.6926(8)	0.3016(4)	0.065(1)
C(53)	0.0036(1)	0.0664(1)	0.2854(7)	0.114(1)
C(54)	0.0058(1)	0.0565(1)	0.3035(8)	0.062(1)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i Z a_j.$$

protonated $[\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3]^+$ groups to satisfy the charge requirements of the complex anion, which is shown in the packing diagram of the title complex (Fig. 2). And this feature appears to be reflected in the ^1H NMR spectra of $\text{NH}_3\text{CH}_2^b\text{CH}_2^c\text{NH}_2^d$ with chemical shifts of 6.29, 3.69, 3.05 and 6.11 for H^a , H^b , H^c and H^d , respectively. The chemical shifts of the ^1H in *o*-aminophenol ligand are in range of 6.59–6.86 ppm.¹⁰

The IR spectra of the dioxo compound show one strong and broad bands with fine structure in range of 886–848 cm^{-1} attributable to the asymmetric and symmetric $\text{Mo}=\text{O}$ stretches, which differs from most of the *cis*-dioxo moiety, but agrees with $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}^2]$ and $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}^4]$ reported in the literature.¹¹ The spectra of the title complex display strong bands at 1475 cm^{-1} and 1256 cm^{-1} which arise from the C–N and C–O stretching vibrations and show a little down shift compared with the 1605 cm^{-1} (C–N) and 1404 cm^{-1} (C–O) stretching vibrations in the *o*-aminophenol molecule because of the coordination of *o*-aminophenol ligand with central metal Mo^{V} ion.

Table 3 Bond lengths (nm)

Mo(1)—N(1)	0.2018(6)	Mo(1)—O(2)	0.2169(6)	Mo(1)—N(3)	0.2007(6)
Mo(1)—O(4)	0.2130(5)	Mo(1)—O(5)	0.1702(6)	Mo(1)—O(6)	0.1709(5)
N(1)—C(11)	0.135(1)	O(2)—C(16)	0.136(1)	N(3)—C(21)	0.137(1)
O(4)—C(26)	0.134(1)	O(41)—C(26)	0.1362(8)	C(11)—C(12)	0.141(1)
C(11)—C(16)	0.139(1)	C(12)—C(13)	0.138(1)	C(13)—C(14)	0.137(2)
C(14)—C(15)	0.145(1)	C(15)—C(16)	0.140(1)	C(21)—C(22)	0.138(1)
C(21)—C(26)	0.138(1)	C(22)—C(23)	0.141(1)	C(23)—C(24)	0.139(1)
C(24)—C(25)	0.142(1)	C(25)—C(26)	0.141(1)	C(31)—C(32)	0.152(1)
C(32)—C(33)	0.149(1)	C(33)—C(34)	0.150(1)	C(41)—C(42)	0.148(2)
C(42)—C(43)	0.145(2)	C(43)—C(44)	0.150(1)	C(50)—C(51)	0.153(3)
C(51)—C(52)	0.138(2)	C(52)—C(53)	0.149(2)	C(53)—C54)	0.146(3)

Table 4 Bond angles (°)

N(1)-Mo(1)-O(2)	75.0(2)	N(1)-Mo(1)-N(3)	167.3(3)	O(2)-Mo(1)-N(3)	94.9(2)
N(1)-Mo(1)-O(4)	94.7(2)	O(2)-Mo(1)-O(4)	79.7(2)	N(3)-Mo(1)-O(4)	75.5(2)
N(1)-Mo(1)-O(5)	100.1(3)	O(2)-Mo(1)-O(5)	88.2(3)	N(3)-Mo(1)-O(5)	87.2(3)
O(4)-Mo(1)-O(5)	157.8(3)	O(1)-Mo(1)-O(6)	87.3(3)	O(2)-Mo(1)-O(6)	160.0(3)
N(3)-Mo(1)-O(6)	101.1(3)	O(4)-Mo(1)-O(6)	92.7(3)	O(5)-Mo(1)-O(6)	104.4(4)
Mo(1)-O(1)-C(11)	116.1(5)	Mo(1)-O(2)-C(16)	111.5(5)	N(1)-C(11)-C(12)	122.5(9)
N(1)-C(11)-C(16)	116.4(8)	C(12)-C(11)-C(16)	121.2(9)	C(11)-C(12)-C(13)	119(1)
C(12)-C(13)-C(14)	119(1)	C(13)-C(14)-C(15)	123(1)	C(14)-C(15)-C(16)	115(1)
O(2)-C(16)-C(11)	114.8(7)	O(2)-C(16)-C(15)	123.4(8)	C(11)-C(16)-C(15)	121.8(8)
Mo(1)-N(3)-C(21)	118.8(5)	Mo(1)-O(4)-C(26)	114.3(5)	N(3)-C(21)-C(22)	122.5(8)
N(3)-C(21)-C(26)	113.9(7)	C(22)-C(21)-C(26)	123.6(9)	C(21)-C(22)-C(23)	117(1)
C(22)-C(23)-C(24)	119(1)	C(23)-C(24)-C(25)	122.0(9)	C(24)-C(25)-C(26)	117.3(8)
O(4)-C(26)-C(21)	116.4(7)	O(4)-C(26)-C(25)	124.1(7)	C(21)-C(26)-C(25)	119.6(8)
C(31)-C(32)-C(33)	111.9(7)	C(32)-C(33)-C(34)	110.5(7)	C(41)-C(42)-C(43)	116(1)
C(42)-C(43)-C(44)	115(1)	C(50)-C(51)-C(52)	110(1)	C(51)-C(52)-C(53)	117(1)
C(52)-C(53)-C(54)	110(1)				

EPR spectra of the powder were recorded at room temperature. The EPR spectrum of the complex is similar to the EPR spectrum presented by flavoenzyme¹². A comparison of the EPR spectra of the complex and flavoenzyme is given in Fig. 3. As shown in the EPR spectrum of flavoenzyme, the signal labeled by letter A is assigned to the ligand of FMN in flavoenzyme and the peak labeled B arises from the field of Mo^V, and the *g* factor of the free d¹ electron indicated by an arrow is 1.97. Similarly, in the EPR spectrum of the title complex, the A signal is attributed to the ligand of *o*-aminophenol and the B peak arises from the field of Mo^V. The *g* factor of the free d¹ electron indicated by an arrow is 1.97 also, the same as that in the EPR spectrum of flavoenzyme. Unlike NMR, IR and UV spectroscopy and electrochemical studies,

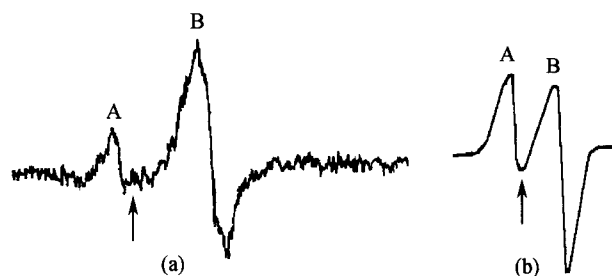


Fig. 3 EPR spectra of $[\text{MoO}_2(\text{HNC}_6\text{H}_4\text{O})_2]^{3-}$ at 288 K (a) and flavoenzyme at 100 K (b).

EPR parameters of the complex in the Mo^V state are essentially invariant with respect to the substituent. The predominant effect which affects the EPR spectra is the structure type of the complex.¹¹ The occurrence of about

the same EPR spectra for the title complex and flavoenzyme suggests that the both substances may have the same coordination feature.

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