

Synthesis and Molecular Structure of Binuclear Tin(IV) Complex Bridged by Terephthalate Anion

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The title complex $[\text{Ph}_3\text{Sn}(\text{CH}_3\text{OH})(\text{terephthalate})(\text{CH}_3\text{OH})\text{SnPh}_3] \cdot 2\text{CH}_3\text{OH}$ was synthesized by the reaction of Ph_3SnCl with terephthalate in the molar ratio of 2:1 in methanol solution and characterized by elemental analysis, IR and ^1H NMR spectra, and the crystal structure was determined by X-ray single crystal diffraction study. The crystal belongs to monoclinic with space group $P2_1/n$, $a = 1.5199(5)$ nm, $b = 0.9000(3)$ nm, $c = 1.8206(6)$ nm, $\beta = 113.970(5)^\circ$, $Z = 2$, $V = 2.2755(13)$ nm³, $D_c = 1.413$ g/cm³, $\mu = 1.146$ mm⁻¹, $F(000) = 980$, $R = 0.0353$, $wR = 0.0606$. In the crystals of complex, the tin atoms rendered five-coordinate in a distorted trigonal bipyramidal structure.

Keywords binuclear, triphenyltin(IV), terephthalate, synthesis, molecular structure

Introduction

Because the polynuclear complexes, consisting of aromatic multi-carboxylic acid and transition metal, have a variety of possible applications ranging from fine retardants to catalysts, and potentially valuable properties reminiscent of zeolites, the study on them has been an active field of coordination chemistry in recent years.¹⁻⁶ By contrast, analogous organo-tin complexes have not been studied extensively,⁷ and their structural chemistry has not been mentioned. Multidentate ligands such as anion of terephthalic acid are capable of forming one-, two-, or three-dimensionally infinite connections between cations and anions.⁸ So the organo-tin complexes bridged by anion of terephthalic acid may be with a bulky variety of

structural features and special biological activities. In order to study the properties and structures of this kind of complexes, complex $[\text{Ph}_3\text{Sn}(\text{CH}_3\text{OH})(\text{terephthalate})(\text{CH}_3\text{OH})\text{SnPh}_3] \cdot 2\text{CH}_3\text{OH}$ was synthesized by the reaction of Ph_3SnCl with terephthalate in the molar ratio of 2:1 in methanol solution and characterized by elemental analysis, IR and ^1H NMR spectra, and the crystal structure was determined by X-ray single crystal diffraction study.

Experimental

Starting materials and instruments

The triphenyltin chloride and terephthalic acid were of analytical grade. Melting points were determined with a Kofler micro melting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer in KBr. ^1H NMR spectra were recorded on a JEOL-FX-90Q spectrometer with TMS as the internal standard and CDCl_3 as the solvent. Elemental analyses were performed on a Carlo-Erba 1106 elemental analyzer.

Synthesis of complex

Anhydrous disodium terephthalate (0.42 g, 2.0 mmol) were added to a methanol solution of Ph_3SnCl (1.54 g, 4.0 mmol). After stirring for 15 h at 40 °C, the reaction mixture was filtered. Solvent was gradually removed by the evaporation under vacuum until solids

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were obtained. The product was recrystallized from methanol and a colorless crystal was given, 1.47 g, yield 76%. m.p. 228–229 °C; ^1H NMR (CDCl_3 , 90 MHz) δ : 4.01 (s, 6H, $2 \times \text{OCH}_3$), 3.85 (s, 6H, $2 \times \text{OCH}_3$), 4.82 (s, 4H, $4 \times \text{OH}$), 7.00–8.23 (m, 34H, $6 \times \text{C}_6\text{H}_5$, $p\text{-C}_6\text{H}_4$); IR (KBr) ν : 3440 (m, OH), 3080, 3046 (m, ph-H), 2971, 2878 (s, C-H), 1632, 1320 (s, CO_2), 576 (w, Sn-C), 465 (m, Sn-O) cm^{-1} ; Anal. calcd for $\text{C}_{48}\text{H}_{50}\text{O}_8\text{Sn}_2$ ($M_r = 992.30$): C 58.10, H 5.08, Sn 23.92; found C 58.49, H 5.22, Sn 23.90.

Determination of crystal structure

A single crystal having approximate dimensions 0.30 mm \times 0.20 mm \times 0.10 mm was mounted on a fiber. All measurements were made on a Bruker smart-1000 CCD diffractometer with graphite monochromated Mo K_α (0.071073 nm) radiation. The data were collected at 293 (2) K to maximum θ value of 25.03°. The crystal belongs to monoclinic with space group $P2_1/n$, $a = 1.5199(5)$ nm, $b = 0.9000(3)$ nm, $c = 1.8206(6)$ nm, $\beta = 113.970(5)^\circ$, $Z = 2$, $V = 2.2755(13)$ nm^3 , $D_c = 1.413$ g/cm^3 , $\mu = 1.146$ mm^{-1} , $F(000) = 980$. The structure was solved by direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined by full-matrix least-squares calculation to $R = 0.0353$, $wR = 0.0606$ for 3988 $R_{\text{int}} = 0.0450$ independent reflections with $I > 2\sigma(I)$. In the final difference map, the residuals are 570 e/nm^3 and -385 e/nm^3 , respectively.

Results and discussion

Selected bond distances and angles are listed in Table 1. The molecular structure of the title complex with the atom numbering scheme is illustrated in Fig. 1. The molecular packing in the unit cell is shown in Fig. 2.

The main feature of the molecular structure is the symmetric binuclear unit made up of two distorted coordination trigonal bipyramids. One oxygen atom from the carboxylate group of terephthalate, one oxygen atom from the coordinated methanol molecule and three carbon atoms respectively from three phenyl groups coordinate to a tin atom so as to form the coordination geometry of a five-coordinated trigonal bipyramidal around the tin atom. The lengths of the Sn(1)—O(1) bond [0.2137(3) nm] and Sn(1)—O(3) bond [0.2516(3) nm] are shorter than the sum of the Van der Waals radii for Sn and O of 0.28 nm. The Sn(1)···O(2) distance of 0.3062 nm is much greater than the sum of the Van der Waals radii for Sn and O. It is shown that the O(2) atom does not make any significant contacts with the Sn(1) atom. It is worthy to take a look at the distances and angles around tin atom in this complex. The bond angles of C(5)—Sn(1)—O(1), C(17)—Sn(1)—O(1) and C(11)—Sn(1)—O(1) are 99.85 (13)°, 100.19 (13)° and 90.87 (13)°, respectively, which are bigger than 90°. On the contrary, the bond angles of C(5)—Sn(1)—O(3) [81.98 (14)°], C(17)—Sn(1)—O(3) [81.53 (15)°] and C(11)—Sn(1)—O(3) [85.07 (15)°] are all smaller than 90°, and O(1)—Sn(1)—O(3) [175.94(11)°] angle significantly deviates

Table 1 Selected interatomic bond distances (nm) and angles (°) for $[\text{Ph}_3\text{Sn}(\text{CH}_3\text{OH})(\text{terephthalate})(\text{CH}_3\text{OH})\text{SnPh}_3] \cdot 2\text{CH}_3\text{OH}$

Sn(1)—C(5)	0.2119(4)	Sn(1)···O(2)	0.3062
Sn(1)—C(17)	0.2119(4)	O(1)—C(1)	0.1296(5)
Sn(1)—C(11)	0.2130(4)	O(2)—C(1)	0.1227(5)
Sn(1)—O(1)	0.2137(3)	O(3)—O(4)	0.2675(5)
Sn(1)—O(3)	0.2516(3)	O(2)—O(4)	0.2755(5)
C(5)—Sn(1)—C(17)	125.20(17)	O(1)—Sn(1)—O(3)	175.94(11)
C(5)—Sn(1)—C(11)	115.59(15)	C(1)—O(1)—Sn(1)	116.7(3)
C(17)—Sn(1)—C(11)	114.50(17)	C(23)—O(3)—Sn(1)	126.7(6)
C(5)—Sn(1)—O(1)	99.85(13)	C(12)—C(11)—Sn(1)	120.7(3)
C(17)—Sn(1)—O(1)	100.19(13)	C(16)—C(11)—Sn(1)	122.1(3)
C(11)—Sn(1)—O(1)	90.87(13)	C(22)—C(17)—Sn(1)	120.8(4)
C(5)—Sn(1)—O(3)	81.98(14)	C(18)—C(17)—Sn(1)	123.2(4)
C(17)—Sn(1)—O(3)	81.53(15)	C(6)—C(5)—Sn(1)	118.2(3)
C(11)—Sn(1)—O(3)	85.07(15)	C(10)—C(5)—Sn(1)	124.7(3)
O(2)—C(1)—O(1)	123.4(4)	O(2)—C(1)—C(2)	121.7(4)

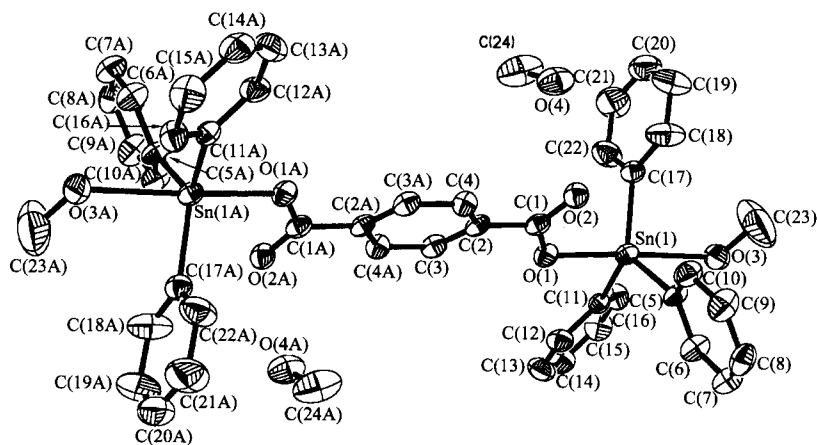


Fig. 1 Molecular structure of the title complex.

from the ideal linear angle. Therefore, the coordination geometry formed by three carbon atoms and two oxygen atoms is a distorted trigonal bipyramidal. However, it is surprising that three carbon atoms from three phenyl groups, two oxygen atoms from one carboxylate group of terephthalate and one coordinated methanol molecule coordinated to a tin atom are found on a face of the trigonal bipyramidal respectively, so the trigonal bipyramidal is a facial isomer.⁹

The crystal consists of the complexes and uncoordinated methanol molecules. The H-bonding exists between the carboxyl groups and uncoordinated methanol molecules as verified by the O(2)—O(4) distance of 0.2755(5) nm and the H-bonding also exists between the coordinated methanol and uncoordinated methanol as verified by the O(3)—O(4) distance of 0.2675(5) nm, so that the complex molecules form the two-dimensional network through the inter-molecular H-bonding (Figs. 1 and 2).

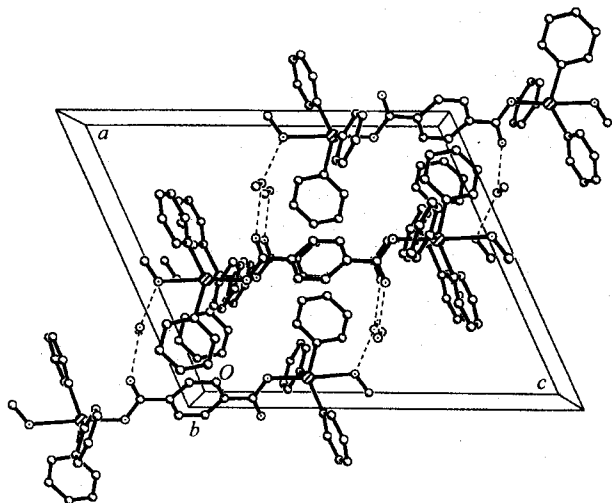


Fig. 2 Projection of the unit cell.

The stretching vibrations observed at 1632 cm^{-1} and 1320 cm^{-1} are attributed to $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ of the carboxylate groups. The $\Delta\nu$ value [$\nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$] of 312 cm^{-1} suggests the monodentate coordination of the carboxylate group,¹⁰ which is also in agreement with the crystal structure as mentioned above.

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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 $\text{Mo K}\alpha$ 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

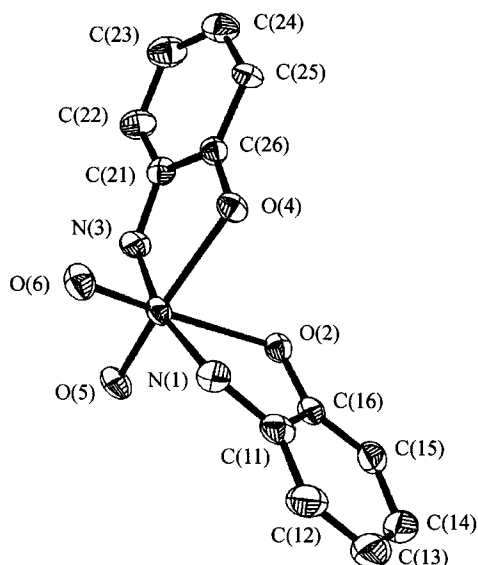
The structure of $[\text{Mo}^{\text{V}}\text{O}_2(\text{HNC}_6\text{H}_4\text{O})_2]^{3+}$ is shown in Fig. 1 and the packing diagram is presented in Fig. 2. The atomic coordinates and thermal parameters are listed in Table 2, while bond lengths and bond angles are tabulated in Tables 3 and 4, respectively.

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($\text{Mo K}\alpha$)	0.071073 nm
Crystal system	orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	$a = 1.4086(3)$ 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 \times 0.30 mm \times 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

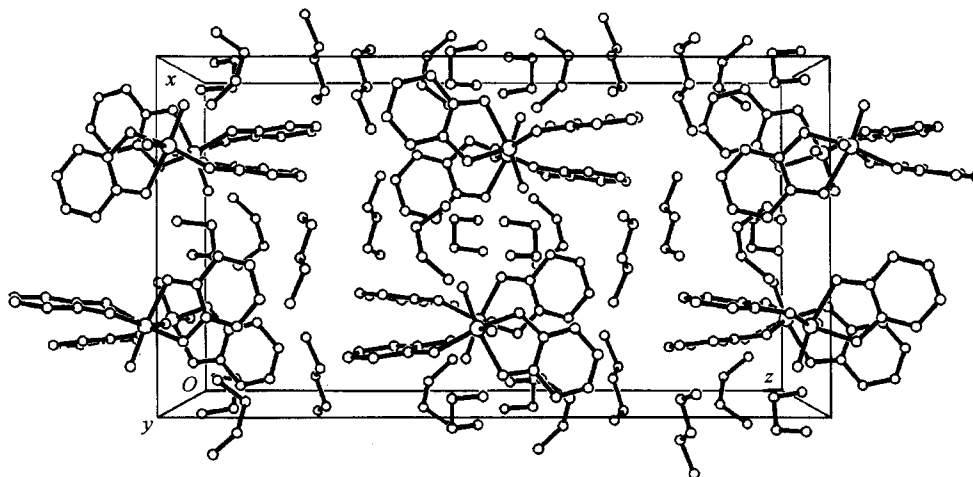


Fig. 2 Packing diagram of the title complex.

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)

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

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)—C(54)	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,

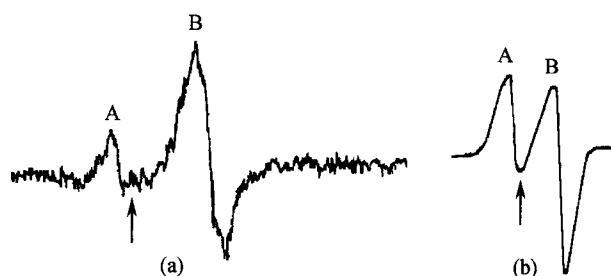


Fig. 3 EPR spectra of $[\text{MoO}_2(\text{HNC}_6\text{H}_4\text{O})_2]^{3-}$ at 288 K (a) and flavoenzyme at 100 K (b).

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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