Inorganica Chimica Acta, 210 (1993) 177–182

A spectroscopic model for the high pH form of sulfite oxidase

Rainer Hahn, Ulrich Küsthardt* and Wolfgang Scherer
Lehrstuhl für Anorganische Chemie I, TU München, Lichtenbergstrasse 4, 85748 Garching (Germany)

(Received March 8, 1993)

Abstract

The syntheses and spectroscopic properties of two monomeric oxo–Mo(V) complexes $[NMe_4][MoO(\mathit{S}C_6H_4–CH{=}\mathit{N}–C_6H_4\mathit{O})(SAr)_2]$ (Ar = Ph (**2a**), $PhCH_3$ (**2b**)) exhibiting a novel S_3NO coordination site are described. The EPR parameters of the Mo(V) complexes are almost identical with the parameters for the high pH form of sulfite oxidase, allowing further predictions for the unknown coordination site of the molybdenum cofactor in such molybdenum-containing enzymes. The Mo(V) compounds react with water to form a μ-oxo-bridged Mo(V) dimer, which is readily oxidized by oxygen to give the monomeric dioxo–Mo(VI) complex $MoO_2(\mathit{S}C_6H_4–CH{=}\mathit{N}–C_6H_4\mathit{O})(sol)$ (**4**) (sol = acetonitrile; dimethyl sulfoxide (DMSO)). The structure of **4** has been determined by X-ray crystallography (space group $P\bar{1}$ (No. 2), $a = 7.855(4)$, $b = 9.530(3)$, $c = 11.676(6)$ Å, $\alpha = 103.96(3)$, $\beta = 99.03(3)$, $\gamma = 100.73(3)°$, $V = 814.5$ Å^3, $\rho_{calc} = 1.79$ g cm^{-3}, $Z = 2$, $R(F) = 0.026$, $R(wF) = 0.026$). The geometry about the molybdenum is distorted octahedral, with two terminal oxo groups *cis* to each other.

Introduction

Molybdenum plays an essential role in the active site of many hydroxylases such as sulfite oxidase, nitrate reductase and xanthine oxidase [1]. All these enzymes contain a common cofactor (Moco). This cofactor is composed of a oxo–molybdenum unit and a pterin-containing ligand system, which is most probably coordinated to the metal through a dithiolene group [2]. The Mo center cycles during enzymatic reaction between the formal oxidation states VI, V and IV. Extended X-ray absorption fine structure (EXAFS) analysis on oxidized enzymes, such as sulfite oxidase, revealed a molybdenum coordination sphere that is comprised of an Mo(VI) center coordinated by two terminal oxo groups (168 pm) — oxidized xanthine oxidase contains one terminal oxygen and one terminal sulfur group — and three sulfur ligands (241 pm) [3]. A nitrogen donor (219 pm) is proposed to complete the pseudo-octahedral coordination sphere as commonly found in dioxo–molybdenum(VI) complexes [4].

Structural investigations on reduced sulfite oxidase (Mo(V)) by EXAFS [3] and EPR [5] techniques led to the proposed structure of the Mo site shown in Fig. 1. Therefore, the molybdenum(V) metal center is coordinated by one terminal oxo ligand (169 pm), one hydroxo group (204 pm), and three sulfur ligands (238 pm). The presence of a sixth ligand is strongly favored as found in many Mo(V) complexes. This ligand is proposed to contain a nitrogen donor atom.

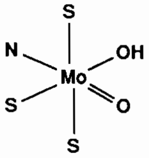

Fig. 1. Schematic view of the molybdenum coordination site in reduced sulfite oxidase.

To our knowledge no oxo–molybdenum(V) compound is known [6] that exhibits a MoO^{3+} core with an S_3NO ligand sphere as assumed for reduced sulfite oxidase. Herein, we present the syntheses and spectroscopic properties of the first complexes of this type.

The following abbreviations will be used throughout the text: acacH = acetylacetone; $mabH_4$ = 2,3 bis(2-mercaptoanilino)butane; $maeH_4$ = 2,3 bis(2-mercaptoanilino)ethane; 8-mqH = 8-mercaptoquinoline; $sipH_2$ = salicylidene(2-hydroxyaniline); $smaH_2$ = *N*-salicylidene-(2-mercaptoaniline); $(sal)_2phenH_2$ = disalicylidene *o*-phenylenediimine; tpz = hydrotris(3,5-dimethyl-1-pyrazolyl)borate; $mPhaeMe_2(LH_2)$ = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptophenyl)ethylenediamine.

Experimental

Materials and methods

All manipulations were performed under argon using standard Schlenk techniques. All solvents were deaer-

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*Author to whom correspondence should be addressed.

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ated, dried and distilled before use. Thiophenol, *p*-thiocresol, acetylacetone, thionyl chloride, tetramethylammonium chloride, salicylaldehyde, aminothiophenol, sodium molybdate and molybdenum(VI) oxide were obtained from Aldrich Chemicals and used without further purification. $MoO_2(acac)_2$ [7], *N*-salicylidene-(2-mercapto)aniline [8], $MoO_2(SC_6H_4CHNC_6H_4O)$ [9] and $[NMe_4][MoO(SAr)_4]$ [10] were prepared according to previously reported syntheses.

EPR spectra were obtained on a JEOL spectrometer JES RE2X at X-band frequency using the ESPRIT 330 data system. The microwave frequency was determined by a R5372 frequency counter (Advantest) and the magnetic field was calibrated with an internal MnO marker. Cyclovoltammetric data were collected using a potentiostat PAR 273 from EG&G. The measurements were controlled and collected by an HP Vectra QS20 using a specially developed CV program [11]. Electronic spectra were measured on an HP 8452A diode array spectrophotometer. IR spectra were obtained using a Perkin-Elmer FT-IR spectrometer (model 1600). Conductivity measurements were carried out on a WTW LF 2000.

Synthesis of $[NMe_4][MoO(SC_6H_4CHNC_6H_4O)(SAr)_2]$ Ar = Ph (2a), (C_6H_4)-p-CH_3 (2b)

A solution of 1.24 g (5.41 mmol) of *N*-salicylidene-(2-mercaptoaniline), $smaH_2$, in 10 ml acetonitrile was added to 3.39 g (5.41 mmol) of $[NMe_4][MoO(SAr)_4]$ (**1**) in 20 ml acetonitrile at room temperature and stirred for 4 h. The color changed from dark blue to deep green. After evaporation of 80% of the solvent and the addition of 100 ml diethyl ether the dark green product precipitated as fine crystals. The precipitate was filtered and washed twice with 50 ml ether. Yield 70%. In solution, **2** is highly sensitive to dioxygen and moisture. *Anal.* **2a**: Found: C, 55.34; H, 4.99; Mo, 15.05; N, 4.40; O, 5.15; S, 15.34. Calc. for $C_{29}H_{31}MoN_2O_2S_3$: C, 55.14; H, 4.95; Mo, 15.19; N, 4.43; O, 5.07; S, 15.23%. *Anal.* **2b**: Found: C, 56.80; H, 5.42; Mo, 14.33; N, 4.21; O, 4.69; S, 14.43. Calc. for $C_{31}H_{35}MoN_2O_2S_3$: C, 56.44; H, 5.35; Mo, 14.54; N, 4.25; O, 4.85; S, 14.58%. UV–Vis: 308 nm ($\epsilon = 27\,180$ l mol^{-1} cm^{-1}), 400 nm ($\epsilon = 5380$ l mol^{-1} cm^{-1}) for **2a** and **2b**. IR (cm^{-1}): ν(Mo=O) **2a**: 923; **2b**: 928. Molar conductivity in acetonitrile of both compounds is 66.27 S cm^2 mol^{-1}.

Formation of MoO_2(sma)DMSO starting from 2a

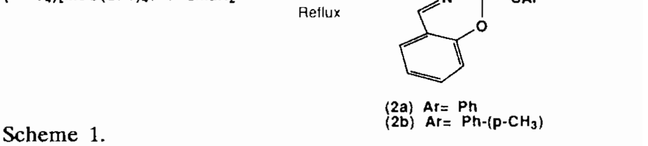
1.25 g (2 mmol) of complex **2a** were dissolved in 10 ml dry and deoxygenated acetonitrile. Slow addition of one equivalent deoxygenated water resulted in a fast reaction. The color turned from dark green to a deep brown solution. Electronic spectra of the solution exhibit a broad band at 453 nm ($\epsilon = 17\,800$ l mol^{-1} cm^{-1}) characteristic for oxo-bridged Mo(V)L dimers. The solution was stirred in air. After 2 h the absorption band at 453 nm disappeared and another transition at 376 nm appeared. The solvent was evaporated and the dark brown product recrystallized from DMSO/H_2O to form a fine solid precipitate (0.66 g, 76%). The product was dissolved in 2 ml DMSO and allowed to stand in a bath of distilled water. Slow diffusion of the water into the solution resulted, after two weeks, in the formation of red crystals.

Crystal structure determination

A red crystal of **4** (size: 0.425×0.375×0.175 mm) was mounted in a capillary on an Enraf-Nonius CAD4 diffractometer with Kappa geometry. Cell constants were determined by centering and least-squares refinement of 25 reflections at high diffraction angles. A total of 5724 reflections was measured in ω-scan. No decay of the crystal could be observed during data collection. The structure was solved by the Patterson method. All atoms were located from subsequent least-squares refinements and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen with isotropic contributions. The weighting scheme of Prince [12] with three refined parameters $P(1) = 0.76$, $P(2) = 0.612$ and $P(3) = 0.603$ was applied at the refinement. All calculations were performed on a DecStation 5000/25 computer using the programs CRYSTALS [13] and PLATON [14].

Results and discussion

The synthesis of mononuclear oxo-molybdenum(V) complexes exhibiting an S_3NO ligand system can be achieved by a substitution reaction starting from the mononuclear precursor $[Mo^VO(SAr)_4]^-$ (**1**) anion (SAr = SC_6H_5, SC_6H_4-*p*-CH_3). The substitution of two arylthiolates by the Schiff base *N*-salicylidene-(2-mercapto)aniline ($smaH_2$) on the Mo^VO^{3+} center results in the formation of the six-coordinated oxo-molybdenum(V) complex with an S_3NO coordination sphere $[MoO(SC_6H_4CHNC_6H_4O)(SAr)_2]^-$ (**2**) anion (Scheme 1). Analytical and spectroscopic data support the proposed structure. Molar conductivity of 66.27 S cm^2



Scheme 1.

mol^{-1} in acetonitrile is characteristic for a 1:1 electrolyte [15]. The mass spectrum of compound **2a** shows the expected isotope pattern at 450 *m*/*e* (anionic field desorption method; ^{98}Mo) corresponding to the fragment $[MoO(SC_6H_4CHNC_6H_4O)(SPh)]^-$. The elimination of one SPh fragment can be explained by the thermolability of complex **2a** and the stability of the S-aryl radical.

The structure of a similar complex, tetramethylammonium-dichloro-oxo-(*N*-salicylidene-2-hydroxyanilino)-molybdate(V) $[NMe_4][(sip)MoOCl_2]$, has been described [16]. This six-coordinated Mo(V) complex has a distorted octahedral geometry. The terminal oxo group and the nitrogen donor atom of the Schiff base ligand are in *trans*-position. Both the chloride ligands are *trans* to each other.

The Mo–O stretching resonances of compounds **2a** and **2b** show the weakening of the Mo–O bond by the sulfur ligand atoms. Comparison with sulfur-free systems (Table 1) demonstrates that the stretching frequency is considerably lower for systems containing two or more sulfur donor atoms. Enhanced π-interactions between metal d-orbitals and empty sulfur d-orbitals decrease the electron density on the MoO^{3+} unit [17].

The electrochemistry of compound **2a** displays a quasi-reversible reduction step at −250 mV versus Ag/AgCl in acetonitrile, indicating formation of a stable Mo(IV) species, presumably $[Mo^{IV}O(SPh)_2(sma)]^{2-}$. Anodic scans result in irreversible oxidation waves at 250, 700 and 800 mV versus Ag/AgCl, respectively. In contrast, cyclovoltammetric studies on the similar complex $[NMe_3][(sma)Mo^VOCl_2]$ show a significantly different redox behavior possessing no reversible reduction wave [18].

EPR measurements confirm the paramagnetic character of **2a** and **2b** as expected for monomeric Mo(V) complexes. The frozen solution spectra at X-band exhibit rhombic type signals with $g_1 = 1.992, g_2 = 1.966, g_3 = 1.954$ and $g_1 = 1.991, g_2 = 1.961, g_3 = 1.953$, for **2a** and **2b** (Fig. 2), respectively. The average g values of **2a** ($\langle g \rangle = 1.967$) and **2b** ($\langle g \rangle = 1.968$) are considerably lower than that of the starting complex $[MoO(SPh)_4]^-$ ($\langle g \rangle = 1.989$). This confirms earlier conclusions [19] that sulfur ligands do cause a significant shift to higher g values compared to those which contain 'harder' ligand atoms like N, O or Cl. Furthermore, we observe an increase in the hyperfine coupling constant $\langle A \rangle$ going from S_4 ($\langle A \rangle = 32.5 \times 10^{-4}$ cm^{-1} for **1**) to S_3NO ($\langle A \rangle = 39.5 \times 10^{-4}$ cm^{-1} for **2a**) coordination.

TABLE 1. Infrared parameters of selected oxo–molybdenum(V) compounds

Compound	ν(Mo=O) (cm^{-1})	Ref.
$[NEt_4][MoOCl_2(sip)]$	940 (nujol)	18
$MoOCl_2(acac)_2$	962 (nujol)	18
$[NEt_4][MoO(mae)]$	898 (nujol)	18
$[NEt_4][MoO(mab)]$	910 (nujol)	18
$[NEt_4][MoO(SPh)_2(sma)]$ (**2a**)	923 (KBr)	herein
$[NEt_4][MoO(SPh\text{-}p\text{-}CH_3)_2(sma)]$ (**2b**)	928 (KBr)	herein

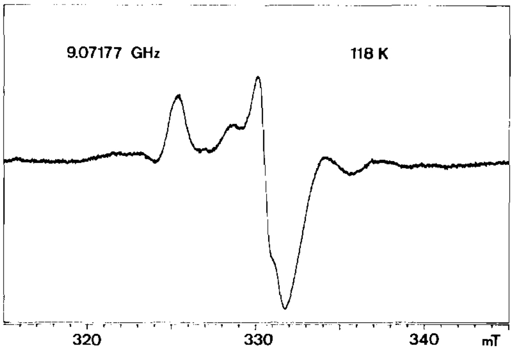


Fig. 2. EPR spectrum of a frozen acetonitrile solution (118 K) of **2b** at X-band frequency (9.07177 GHz).

The EPR parameters of our monomeric Mo(V) complexes (**2a** and **2b**) are in excellent agreement with those found for sulfite oxidase in its high pH Mo(V) state ($g_1 = 1.987, g_2 = 1.964, g_3 = 1.953$) [5]. The g values differ only by 0.001–0.005 units expressing similar coordination sites in the model compounds. Table 2 summarizes the EPR data of **2a, 2b** and selected Mo(V) complexes as well as EPR data of sulfite oxidase.

In a first approximation it is possible to establish a dependence of mean g values on the composition of the coordination sphere around the Mo^VO core. 'Hard' donor atoms such as Cl and O shift the g value to higher field, with chloride exhibiting a smaller influence than oxygen donor atoms. 'Soft' donor atoms such as sulfur and nitrogen shift the EPR signal to higher g values. The influence of sulfur, as a better π-acceptor, is considerably higher than that of nitrogen. However, complexes such as $MoO(tpz)(SPh)_2$ and $MoOCl(8\text{-}mq)_2$ result in similar mean g values as observed for S_3NO coordination sites. Therefore, conclusions about the exact coordination sphere (set of donor atoms, geometrical constraints and electronic properties) cannot be drawn comparing mean g values exclusively.

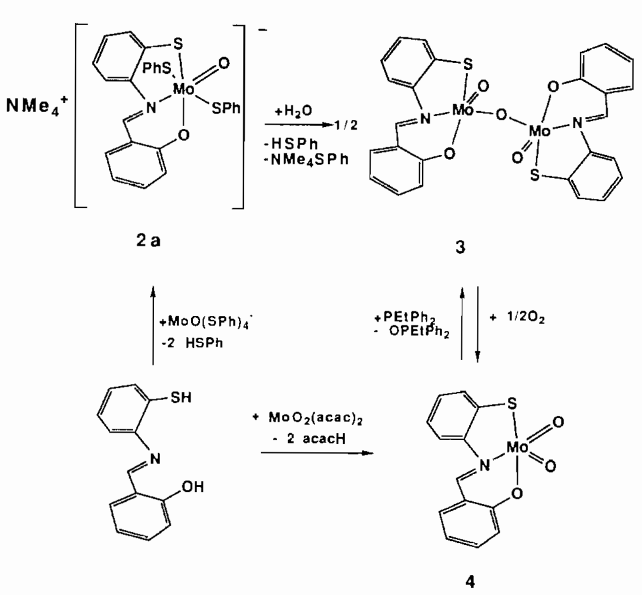
Up to now, no Mo(V) compound was known that models almost exactly the anisotropic EPR parameters of molybdenum hydroxylases. Therefore, predictions of the structure of the active site in such enzymes, using EPR spectroscopy, were limited. For the first time, Mo(V) model complexes are available that allow more precise conclusions about the Mo coordination site in reduced sulfite oxidase (high pH form). We therefore propose a S_3NO set of donor atoms on the MoO^{3+} core, which independently conforms with the EXAFS measurements performed on reduced sulfite oxidase (Mo(V)).

TABLE 2. EPR parameters of complexes **2a**, **2b** and related Mo(V) compounds as well as sulfite oxidase

Complex	Coord. type[a]	$\langle g \rangle$	$\langle A \rangle$[b]	g_1	A_1[b]	g_2	A_2[b]	g_3	A_3[b]	Ref.
trans-MoOCl(acac)	ClO_4	1.938	49.0	1.950	33.4	1.940	36.2	1.927	77.6	16
trans-MoOCl(sal)$_2$(phen)	N_2ClO_2	1.940	44.1	1.955	25.0	1.926	33.4	1.947	71.5	16
[MoO(sma)Cl$_2$]$^-$	$SNOCl_2$	1.955	43.5	1.971	67.4	1.947	31.5	1.947	31.5	18
MoO(tpz)(SCH$_2$CH$_2$O)	SN_3O	1.961	38.0	1.992		1.965		1.932		19
MoO(tpz)(SPh)$_2$	S_2N_3	1.967	35.8	2.004	50.0	1.979	11.0	1.973	40.0	19
[MoO(sma)(SPh)$_2$]$^-$ (**2a**)	S_3NO	1.967	39.5	1.992	64.0	1.966	15.0	1.954	38.0	herein
[MoO(sma)(SPhCH$_3$)$_2$]$^-$ (**2b**)	S_3NO	1.968	39.6	1.991	65.0	1.961	15.0	1.953	39.0	herein
MoOCl(8-mq)$_2$	S_2N_2Cl	1.969	38.8	2.003	58.4	1.950	20	1.948	38.5	20
cis-[MoO(SH)L]$^-$	S_3N_2	1.977	38.0	2.016		1.961		1.953		21
[MoO(mab)]$^-$	S_2N_2	1.986	33.0	2.004	50.0	1.979	11.0	1.973	40.0	22
[MoO(SPh)$_4$]$^-$ (**1**)	S_4	1.989	32.5	2.015		1.980				10
Sulfite oxidase (high pH form)		1.968		1.987		1.964		1.953		5, 23

[a]Terminal oxygen atoms excluded. [b]Units: 10^{-4} cm^{-1}.

The reactivity of the monomeric Mo(V) complex **2a** has been studied in detail. Its anion is very sensitive to traces of water. Upon addition of argon saturated water, the green solution turns brown in seconds. The formation of thiophenol in the reaction mixture can be detected by GC/MS. The reaction has been followed by electronic spectroscopy. The monomeric Mo(V) complex **2a** exhibits an absorption band at 596 nm ($\epsilon = 2850$ l mol^{-1} cm^{-1}). Upon reaction with water this transition disappears and a new absorption band at 462 nm rises, characteristic for dimeric μ-oxo species [24]. At the same time, the EPR signal of **2a** completely disappears. The IR spectrum (KBr) of the product still exhibits a band at 948 cm^{-1} assigned to a mono-oxo species. Formation of the dimeric Mo(V) complex, (μ-O)[Mo^{V}O(sma)]$_2$ (**3**), upon reaction of (sma)Mo^{VI}O$_2$ (**4**) with phosphines, has been reported earlier [24]. Comparison of the spectroscopic data published therein with an authentic sample of **3** clearly supports its formation upon hydration reaction of **2a** (Scheme 2).



Scheme 2.

Exposure of **3** in acetonitrile to air results in formation of the known mononuclear Mo(VI) complex, (sma)Mo^{VI}O$_2$ (**4**), as proved by various spectroscopic and analytical methods [9]. The reaction can be followed by UV–Vis spectroscopy. The absorption band correlated to the dinuclear compound disappears and a new transition at 370 nm is observed. Red–brown crystals of **4** were obtained by recrystallization from DMSO and were characterized crystallographically.

A view of the structure of (sma)Mo^{VI}O$_2$·DMSO (**4**) is presented in Fig. 3. Crystal, data collection and refinement parameters are listed in Table 3. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 4. Selected distances and angles are listed in Table 5. An analogous structure exhibiting a sulfonate-substituted *N*-salicylidene-(2-mercaptoaniline) ligand has been reported by Holm and co-workers [24].

The MoO$_2^{2+}$ core dominates the considerably distorted octahedral geometry. The two terminal oxo groups (O(2) and O(3)) are *cis* to each other and exhibit typical Mo–O double bond distances (Mo–O(2) 170.3, Mo–O(3) 170.1 pm). The Mo–N(1) and Mo–O(4) distances (both 231.2 pm) are considerably elongated due to the strong *trans* effect of the two terminal oxo groups. The usually planar Schiff base ligand system is slightly twisted. The angle between the two planes defined by the six C atoms of each phenyl ring is 18.5°. The Mo–S(1) distance (241.0 pm) falls into the typical range of molybdenum–sulfur single bond distances as found in many Mo(VI) complexes [25].

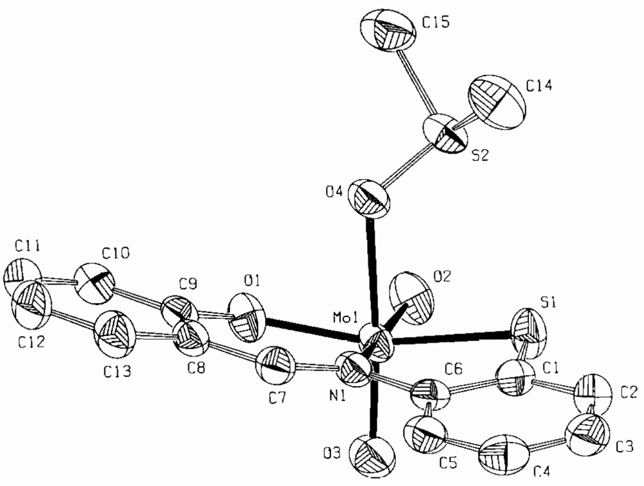


Fig. 3. Crystal structure of (sma)$Mo^{VI}O_2$ (4), without hydrogen atoms. Thermal ellipsoids of the PLATON presentation correspond to 50% probability.

TABLE 3. X-ray crystallographic data of **4**

Formula	$C_{15}D_6H_9MoN_1O_4S_2$
Crystal system	triclinic
Space group	$P\bar{1}$, Int. Tables No. 2
a (Å)	7.855(4)
b (Å)	9.530(3)
c (Å)	11.676(6)
α (°)	103.96(3)
β (°)	99.03(3)
γ (°)	100.73(3)
V (Å^3)	814.5
Z	2
ρ_{calc} (g cm^{-3})	1.79
T (°C)	$+23\pm1$
Radiation	Mo Kα ($\lambda=0.7107$ Å)
Monochromator	graphite
μ (cm^{-1})	10.5
Scan type	ω
Scan range (°)	$1.1+0.25\tan\theta$
No reflections collected	5724
No. independent reflections	2605
No. reflections used in refinement	2574 ($I>2.0\sigma(I)$)
Standard reflections	3 for intensity check every 60 min 3 for orientation check every 200 reflections
$R(F)$ (%)	2.6
$R(wF)$ (%)	2.6
$D(r)$ (e Å^3)	+0.64 0.91 Å from Mo
$\Delta(\rho)$	−0.59

TABLE 4. Final coordinates and equivalent isotropic thermal parameters for **4**

Atom	x/a	y/b	z/c	U_{eq}[a] (Å^2)
Mo(1)	0.14947(2)	0.24121(2)	0.29579(1)	0.0326
S(1)	0.38873(8)	0.39499(6)	0.24389(5)	0.0456
S(2)	0.53900(6)	0.28538(6)	0.47577(4)	0.0392
O(1)	0.0294(2)	0.0624(2)	0.3299(1)	0.0436
O(2)	0.1715(2)	0.3773(2)	0.4257(1)	0.0491
O(3)	−0.0205(2)	0.2628(2)	0.1968(2)	0.0516
O(4)	0.3800(2)	0.1652(2)	0.3936(1)	0.0421
N(1)	0.2085(2)	0.0728(2)	0.1369(1)	0.0324
C(1)	0.4010(3)	0.2804(2)	0.1045(2)	0.0371
C(2)	0.5102(3)	0.3418(3)	0.0363(2)	0.0438
C(3)	0.5183(3)	0.2609(3)	−0.0760(2)	0.0496
C(4)	0.4206(3)	0.1152(3)	−0.1222(2)	0.0468
C(5)	0.3178(3)	0.0508(3)	−0.0548(2)	0.0404
C(6)	0.3077(2)	0.1316(2)	0.0598(2)	0.0330
C(7)	0.1514(3)	−0.0690(2)	0.1123(2)	0.0368
C(8)	0.0559(2)	−0.1502(2)	0.1811(2)	0.0352
C(9)	0.0038(2)	−0.0851(2)	0.2861(2)	0.0346
C(10)	−0.0809(3)	−0.1749(3)	0.3488(2)	0.0466
C(11)	−0.1144(3)	−0.3270(3)	0.3065(2)	0.0537
C(12)	−0.0664(3)	−0.3947(3)	0.2013(3)	0.0560
C(13)	0.0176(3)	−0.3072(2)	0.1386(2)	0.0477
C(14)	0.7249(4)	0.2566(5)	0.4126(3)	0.0656
C(15)	0.5889(4)	0.2184(3)	0.6037(2)	0.0598

[a] Equivalent isotropic thermal parameter U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5. Selected distances (pm) and angles (°) for MoO_2(sma)·DMSO

Mo–S(1)	241.0(1)
Mo–O(1)	194.9(1)
Mo–O(2)	170.3(1)
Mo–O(3)	170.1(2)
Mo–O(4)	231.2(1)
Mo–N(1)	231.2(2)
O(1)–Mo–S(1)	154.94(5)
O(2)–Mo–S(1)	89.60(6)
O(2)–Mo–O(1)	103.50(7)
O(3)–Mo–S(1)	97.88(6)
O(3)–Mo–O(1)	99.05(7)
O(3)–Mo–O(2)	105.33(8)
O(4)–Mo–S(1)	82.43(4)
O(4)–Mo–O(1)	76.87(6)
O(4)–Mo–O(2)	87.98(7)
O(4)–Mo–O(3)	166.68(7)
N(1)–Mo–S(1)	78.70(4)
N(1)–Mo–O(1)	83.48(6)
N(1)–Mo–O(2)	163.24(7)
N(1)–Mo–O(3)	88.28(7)
N(1)–Mo–O(4)	78.70(5)

Supplementary material

Tables of atom positions, anisotropic displacement parameters, and bond distances for all atoms and a listing of calculated and observed structure factors (27 pages) are all available from author W.S. For further details of the crystal structure determination, the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen (Germany) may be contacted, quoting the reference to this paper, the names of the authors, and the CSD number CSD-57413.

Acknowledgement

Financial support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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