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New dinuclear thiobenzoato complexes of molybdenum(V) containing Mo₂O₂S₂ core. X-ray crystal structures of [Mo₂O₂S₂(OSCC₆H₅)₂(py)₂] and [Mo₂O₂S₂(OSCC₆H₅)₂(γ-pic)₂]·2H₂O

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Marina Cindrić, Višnja Vrdoljak, Biserka Prugovečki and Boris Kamenar*

Laboratory of General and Inorganic Chemistry, Chemistry Department, Faculty of Science, University of Zagreb, Ulica kralja Zvonimira 8, POB 153, 10001 Zagreb, Croatia

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Abstract—The $[Mo_2O_2S_2(OSCC_6H_5)_2]$ (1) has been prepared either by the reaction of $[Mo_2O_3(C_5H_7O_2)_4]$ or of $[Mo_4Cl_2O_6(O_2CCH_3)_6]$ ·(CH₃CO)₂O with thiobenzoic acid. The product was then used to prepare two complexes of the general formula $[Mo_2O_2S_2(OSCC_6H_5)_2L_2]$ (where L = pyridine (2) or γ -picoline (3)). All complexes were characterized by elemental analyses, IR spectra and magnetic measurements. The structures of (2) and (3) were proved by X-ray structure analysis. Both complexes are dinuclear containing $Mo_2O_2S_2$ core with two Mo atoms linked by a Mo–Mo single bond. The Mo atoms are octahedrally coordinated by oxo-oxygen, two bridging sulfido-sulfurs, one pyridine (or γ -picoline)-nitrogen and thiobenzoato-sulfur and thiobenzoato-oxygen atoms. \mathbb{O} 1998 Elsevier Science Ltd. All rights reserved

Keywords: crystal structure; molybdenum(V) complexes; thiobenzoato complexes; dimeric structure.

Relevance of molybdenum(V) complexes containing Mo–S bonding to the molybdoenzymes is well known and extensively studied [1–4]. This is particularly true due to the suggestion that the molybdoenzymes in the oxidized forms such as xanthine oxidase and sulfite oxidase contain oxo-molybdenum cores with the molybdenum atom coordinated by two or more sulfur ligands. The usual octahedral surroundings about molybdenum atoms in such systems are commonly completed by the additional nitrogen donor ligands [5]. In addition, interest in Mo–S chemistry has also grown due to the implication of this metal in the catalytic hydrodesulfurization processes [6, 7].

In this paper we describe the synthesis and structural characterization of three new complexes containing MoS_2Mo bridging core with thiobenzoato ligands as simultaneous oxygen and sulfur donors. Two of them with additional pyridine and γ -picoline as nitrogen donor ligands. Similar dinuclear di- μ -oxo and μ -oxo- μ -sulfido molybdenum(V) complexes of the formulae $[Mo_2O_3X(OSCC_6H_5)_2]_n$ and $[Mo_2O_3X(OSC$ $C_6H_5)_2(py)_2$] (X=O or S) have been prepared by M. Rakowski DuBois in 1978 but their structures have never been determined by X-ray diffraction method [8]. They were prepared using molybdenum(VI) compounds, MoO₂Cl₂ and Na₂MoO₄.

EXPERIMENTAL

The starting acetylacetonato $[Mo_2O_3(acac)_4]$ [9] and acetato $[Mo_4Cl_2O_6(O_2CCH_3)_6]$ ·(CH₃CO)₂O [10] complexes were prepared as described earlier. Reagent grade solvents and all other chemicals were used without further purification.

The IR spectra of KBr pellets were recorded on a FTIR 1600 Fourier-transform spectrometer in the $4500-450 \text{ cm}^{-1}$ region. Magnetic measurements were carried out at room temperature using Gouy method.

Preparation of $[Mo_2O_2S_2(OSCC_6H_5)_2]$ (1)

Procedure (*i*). A mixture of $[Mo_2O_3(acac)_4]$ (1 g, 1.57 mmol) and thiobenzoic acid (1.8 g, 13.03 mmol) in dichloromethane (10 cm³) was heated for 2 hours.

^{*} Author to whom correspondence should be addressed.

The resulting red-brown precipitate was filtered and washed with dichloromethane and methanol. Yield: 0.5 g, 57%.

Procedure (ii). The same product was prepared by warming a mixture of $[Mo_4Cl_2O_6(O_2CCH_3)_6]$. $(CH_3CO)_2O (0.25 \text{ g}, 0.25 \text{ mmol})$ with thiobenzoic acid (0.35 g, 2.53 mmol) in dichloromethane (10 cm^3) for 45 min. After 2 days at room temperature red-brown product was isolated. Yield: 0.25 g, 86%. Found: C, 29.97; H, 1.58; Mo, 34.18; S, 22.16. Calc. for $C_{14}H_{10}Mo_2O_4S_4$: C, 29.90; H, 1.79; Mo, 34.12; S, 22.81%. IR (cm⁻¹): 3061w, 1592m, 1455s, 1421s, 1310m, 1230s, 1175s, 974s, 937s, 839s, 678s, 475m.

Preparation of $[Mo_2O_2S_2(OSCC_6H_5)_2(py)_2]$ (2)

Pyridine (1.5 cm^3) was added to a suspension of $[Mo_2O_2S_2(OSCC_6H_5)_2]$ (0.15 g, 0.27 mmol) in dichloromethane (15 cm³) and the reaction mixture warmed

up for 15 min. After three days an orange-red crystalline product was isolated. Yield: 0.05 g, 26%. Found: C, 40.12; H, 2.75; Mo, 27.06; N, 3.36; S, 17.93. Calc. for $C_{24}H_{20}Mo_2N_2O_4S_4$: C, 40.0; H, 2.80; Mo, 26.63; N, 3.89; S, 17.80%. IR (cm⁻¹): 3065m, 1595m, 1460s, 1446s, 1435s, 1309m, 1248s, 1220s, 1012m, 978s, 940s, 469m.

Preparation of $[Mo_2O_2S_2(OSCC_6H_3)_2(\gamma-pic)_2]\cdot 2H_2O$ (3)

Analogously as above, to a suspension of $[Mo_2O_2S_2(OSCC_6H_5)_2]$ (0.15 g, 0.27 mmol) in dichloromethane (10 cm³) γ -picoline was added and the reaction mixture warmed up for 15 min. From the resulting solution after three days an orange crystalline product was isolated. Yield: 0.05 g, 25%. Found: C, 39.29; H, 3.79; Mo, 24.67; N, 3.91; S, 16.01. Calc. for C₂₆H₂₈Mo₂N₂O₆S₄: C, 39.80; H, 3.60; Mo,

Table 1. Crystal data for $[Mo_2O_2S_2(OSCC_6H_5)_2(py)_2]$ (2) and $[Mo_2O_2S_2(OSCC_6H_5)_2(\gamma\text{-pic})_2]\cdot 2H_2O$ (3)

	2	3
Formula	$C_{24}H_{20}Mo_2N_2O_4S_4$	$C_{26}H_{28}Mo_2N_2O_6S_4$
Mol. wt	720.54	784.62
Crystal size (mm)	$0.25 \times 0.20 \times 0.35$	$0.20 \times 0.10 \times 0.55$
Colour	red	orange-red
a (Å)	14.453(3)	13.917(2)
b (Å)	10.256(2)	9.822(1)
<i>c</i> (Å)	18.547(3)	24.781(6)
α (°)	90	90
β (°)	97.32(3)	102.36(2)
γ (°)	90	90
$V(Å^3)$	2726.8(9)	3308.9(10)
Crystal system	monoclinic	monoclinic
Ζ	4	4
$d_{\text{calc.}} (\text{gcm}^{-3})$	1.755	1.575
Space group	C2/c	$P2_{1}/c$
Temp. (°C)	23	23
Scan method	Θ–2Θ	ω
2\O range (°)	4–60	4–60
hkl range	$\pm 20, +14, +26$	$\pm 19, \pm 13, \pm 34$
Max time/rfln(h)	1.5	2
μ (Mo- K_{α})	12.59	10.49
(cm^{-1})		
Data measured	4320	9965
Unique data	3993	9395
Observed data $[I > 2\sigma(I)]$	1600	2575
Number of variables	163	361
Max/min $\Delta \rho$ (e ³ /Å ³)	0.663 / -0.802	1.337 / -1.274
$R1^a$ for rfln. with $I > 2\sigma(I)$	0.062	0.094
$wR2^b(F_o^2)$	0.148	0.243
$GooF^c$	0.918	0.916

^{*a*} $R1 = \Sigma ||F_c| - |F_c|| / \Sigma |F_o|.$

^{*b*} $wR2 = [\Sigma w(F_o - F_c)^2 / \Sigma wF_o^2]^{1/2}, w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], a = 0.0587 \text{ for } 2, a = 0.0934 \text{ for } 3, b = 0.00 \text{ for } 2 \text{ and } 3, P = (\max(F_o^2 \text{ or } 0) + 2F_c^2)/3.$

^c GooF = S = $[\Sigma w (F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$.

24.45; N, 3.57; S, 16.34%. IR (cm⁻¹): 3067m, 1618s, 1595m, 1462s, 1435s, 1307m, 1235s, 1025m, 978s, 944s, 465m.

X-ray crystallography

Intensity data were collected at 293 K by using graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.7107$ Å) on a STOE updated Philips PW1100 diffractometer. Three standard reflections were monitored periodically. Intensity variations of 8.9% (2) and 9.9% (3) were observed and consequently corrected for in the data reduction. The intensities were reduced to Fo by applying corrections for Lorentz and polarization effects. Absorption corrections were not applied.

The structures of both compounds were solved by using direct methods implemented in SIR92 programs [11] and succesive Fourier syntheses. The refinements were performed by full matrix least squares method assuming anisotropic temperature factors for all non-H atoms using SHELXL96 [12] program. All hydrogen atoms, except those belonging to the water molecules, were calculated on the geometrical ground and treated with the constrained lengths in the refinement. Hydrogen atoms of water molecules were not located. Crystal parameters, data collection details for both compounds and the results of the refinements are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Crystals of **3** were extremely fragile thus causing difficulties to manipulate with them. They cracked very easily. This is most probably the reason for relatively high reliability index for the structure of **3**. The distances and angles were calculated by SHELXL96 and PARST [13] program, the molecular and crystal structures by ORTEP-3 [14]. All calculations were performed on an IBM PC/AT compatible microcomputer (processor 80486/ 66 MHz).

Tables with complete interatomic distances and angles, positional and anisotropic thermal parameters, and observed and calculated structure factors for the two structures have been deposited with the Editor, from whom copies are available on request.

RESULTS AND DISCUSSION

The complex **1** was prepared by two alternative ways, either by the reaction of $[Mo_2O_3(C_5H_7O_2)_4]$ or of $[Mo_4Cl_2O_6(O_2CCH_3)_6] \cdot (CH_3CO)_2O$ with thiobenzoic acid. The product was stable and insoluble in all common solvents suggesting its polynuclear nature $[Mo_2O_2S_2(OSCC_6H_5)_2]_n$ rather with six than five-coordinated molybdenum atom. The complex containing five-coordinated molybdenum would be unsaturated and therefore more reactive. Its IR spectrum supports such structure: strong broad band at 839 cm^{-1} is indicative for an intermolecular metal... oxygen interaction $(Mo=O\cdots Mo=O\cdots)$ the same as it has been observed for $[Mo_2O_4(OSCC_6H_5)_2]_n$ at 830 cm^{-1} [8]. Due to its insolubility we were not able to prepare

Table 2. Selected bond lengths (Å) and angles (°) for $[Mo_2O_2S_2(OSCC_6H_5)_2(py)_2]$ (2) and $[Mo_2O_2S_2(OSCC_6H_5)_2(\gamma - pic)_2] \cdot 2H_2O$ (3)

2		3			
Mol-Ol	1.685(5)	Mo11-O11	1.679(8)	Mo21-O21	1.684(8)
Mol-O2	2.257(4)	Mo11-O12	2.263(8)	Mo21-O22	2.270(7)
Mol-N1	2.305(5)	Mo11-N11	2.279(8)	Mo21-N21	2.272(8)
Mol-Sl	2.310(2)	Mo11-S11	2.316(3)	Mo21-S11	2.321(3)
Mol-Sl'	2.322(2)	Mo11-S12	2.314(3)	Mo21-S21	2.318(3)
Mo1–S2	2.580(2)	Mo11-S12	2.567(3)	Mo21-S22	2.579(3)
Mol-Mol'	2.822(1)	Mo11-Mo21	2.831(1)		
Ol-Mol-Nl	86.9(2)	O11-Mo11-N11	87.2(3)	O21-Mo21-N21	88.2(3)
O2-Mo1-N1	76.1(2)	O12-Mo11-N11	74.4(3)	O22-Mo21-N21	75.7(3)
O1-Mo1-S1	107.8(2)	O11-Mo11-S11	108.6(3)	O21-Mo21-S21	107.4(3)
O2-Mo1-S1	88.37(12)	O12-Mo11-S11	89.7(2)	O22-Mo21-S21	91.8(2)
N1-Mo1-S1	84.3(2)	N11-Mo11-S11	85.1(2)	N21-Mo21-S21	84.4(2)
O1-Mo1-S1'	103.4(2)	O11-Mo11-S21	104.4(3)	O21-Mo21-S11	104.2(3)
O2-Mo1-S1'	90.63(11)	O12-Mo11 -S21	90.4(2)	O22-Mo21 -S11	88.8(2)
S1-Mo1-S1'	102.31(7)	S21-Mo11-S11	101.96(11)	S21-Mo21-S11	101.68(10)
O1-Mo1-S2	97.4(2)	O11-Mo11-S12	95.3(3)	O21-Mo21-S22	95.1(3)
O2-Mo1-S2	62.90(11)	O12-Mo11-S12	62.9(2)	O22-Mo21-S22	62.5(2)
N1-Mo1-S2	81.76(14)	N11-Mo11-S12	81.0(2)	N21-Mo21-S22	81.9(2)
S1-Mo1-S2	150.33(7)	S11-Mo11-S12	151.72(11)	S21-Mo21-S22	153.14(12)
S1'-Mo1-S2	86.20(7)	S21-Mo11-S12	86.00(11)	S11-Mo21-S22	86.25(10)
Mol-Sl-Mol'	75.08(6)	Mo11-S11-Mo21	75.25(9)	Mo11-S21-Mo21	75.34(10)

suitable crystals to prove this structure also by the Xray diffraction method. The formation of the MoS_2Mo bridge may be explained by the apperance of H_2S produced *in situ* from the molybdenum catalyzed hydrolysis of thiobenzoic acid. The analogous observations have been made also in preparing some other molybdenum(V) complexes with thio-ligands [15–18]. The strong donor ligands such as pyridine or γ -picoline stabilized the dinuclear structures producing complexes **2** and **3**.

The structures of $[Mo_2O_2S_2(OSCC_6H_5)_2(py)_2]$ (2) and $[Mo_2O_2S_2(OSCC_6H_5)_2(\gamma-pic)_2]\cdot 2H_2O$ (3) are built up of dinuclear complex molecules as shown in Fig. 1. However, while the molecular structure of the **2** has crystallographically imposed two-fold symmetry axis the structure **3** exhibits a pseudo two-fold symmetry. The octahedral coordination about each molybdenum atom within a dimer is considerably distorted with the angles ranging from 76.1(2) to $107.8(2)^{\circ}$ in **2** and from 74.4(3) to $108.6(3)^{\circ}$ in **3**. The distances between two Mo atoms of 2.822(1) in **2**, and 2.831(1) Å in **3** are indicative of a single Mo–Mo bond [19, 20]. The observed diamagnetism of these complexes suggests a strong metal-metal interactions. In both compounds the two molybdenum atoms are bridged *via* two sulfur atoms with average values for the Mo–S_{br} bond lengths





(b)

Fig. 1. ORTEP-3 illustration of the structures of (a) $[Mo_2O_2S_2(OSCC_6H_5)_2(py)_2]$ (2) and (b) $[Mo_2O_2S_2(OSCC_6H_5)_2(py)_2] \cdot (2)$ and (b) $[Mo_2O_2S_2(OSCC_6H_5)_2(py)_2] \cdot (2)$ (3) showing the atom numbering schemes and thermal ellipsoids (50%) for the atoms. The H atoms are unlabelled.

of 2.316(2) Å in 2 and of 2.315(3) Å in 3, respectively [17, 21]. The four-membered rings of the Mo_2S_2 bridging core are not planar but folded along the lines connecting two bridging sulfur atoms: the dihedral angles between two SMoS planes are 158.35(0) and $157.2(2)^{\circ}$ in 2 and 3, respectively. The Mo=O bond lengths of 1.685(5), and 1.679(8) and 1.684(8) Å for 2 and 3, respectively are normal values for such bond to the terminal oxo-oxygen atoms [22]. The Mo-S bond lengths [2.580(2) in (2), 2.567(3) and 2.579(3) Å in 3] as well as the Mo–O bond lengths [2.257(4) in 2, 2.263(8) and 2.270(7) Å in 3] from the thiobenzoato ligands are in good agreement with the values found for such bonds in similar molybdenum(V) structures [23-25]. The molybdenum-to-thiobenzoato-oxygen bond lengths are lengthened due to the trans influence of the terminal oxo-oxygen atoms. The same applies to the molybdenum-to-thiobenzoato sulfur and molybdenum-to-nitrogen bonds [2.305(5) in 2, 2.279(9) and 2.272(8) Å in 3] owing to their *trans* positions to the bridging sulfido-sulfur atoms [26, 27]. Bond lengths and angles within thiobenzoato ligands, pyridine and γ -picoline are within expected values.

Two water molecules in **3** are hydrogen-bonded to each other having O1w...O2w distance amounting to 2.76(1) Å. Otherwise there are no any other than van der Waals interactions between the complex and water molecules.

The IR spectra of all three complexes confirm the presence of C–S group at 937 (complex 1), 940 (2) and 944 cm⁻¹(3), as well as of the C–O group at 1445 (complex 1), 1460 (2) and 1462 cm⁻¹ (3), respectively. The strong apsorption maxima at 974 and 475 (complex 1), 978 and 469 (2), 978 and 465 cm⁻¹ (3), belong to the Mo–O (terminal) and Mo–S (bridging) stretching frequencies, respectively [8, 17, 28].

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