ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 4, pp. 195–199. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © P.L. Sinkevich, V.S. Korenev, P.A. Abramov, A.V. Rogachev, Yu.A. Laricheva, M.A. Mikhailov, A.L. Gushchin, M.N. Sokolov, 2014, published in Koordinatsionnaya Khimiya, 2014, Vol. 40, No. 4, pp. 195–199.

Synthesis and Crystal Structure of the Binuclear Complex $Cs_3[Mo^V_2O_2(\mu\text{-}S)_2Cl_4(H_2O)_2]Cl$

P. L. Sinkevich[a], **V. S. Korenev**[a, b, *], **P. A. Abramov**[a, b], **A. V. Rogachev**[a], **Yu. A. Laricheva**[a], **M. A. Mikhailov**[a], **A. L. Gushchin**[a, b], **and M. N. Sokolov**[a, b]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia*

[b] *Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia*

**e-mail: wkorenev@niic.nsc.ru*

Received August 4, 2013

Abstract—The destruction of hydroxy and aqua bridges of the cyclic pentamer $K_2I_2[Mo_{10}O_{10}(\mu\text{-}S)_{10}(OH)_{10}(H_2O)_5] \cdot 20H_2O$ (**I**) in HCl in the presence of CsCl gave a new binuclear oxothiomolybdenic complex $Cs_3[Mo_2O_2(\mu\text{-}S)_2Cl_4(H_2O)_2]Cl$ (**II**), which was isolated and characterized by X-ray crystallography. The dimeric fragment in complex **II** consists of two distorted octahedral Mo(V) centers, which have nonequivalent environment and are connected by two sulfide bridges. The Mo–Mo distance (2.8411(6) Å) in **II** corresponds to a metal–metal bond.

DOI: 10.1134/S1070328414040095

INTRODUCTION

The transition metal sulfide complexes demonstrate unusually broad range of stoichiometries, coordination geometries, and oxidation states. The demand for these systems from bioinorganic chemistry [1] and catalysis [2] is related to their ability to be involved in electron and proton transfer. Since the early 1980s, the number of publications on the synthesis and characteristics of molybdenum and tungsten complexes with sulfide ligands has steadily grown [3–8]. The development of the thiomolybdate chemistry is also stimulated by the petroleum production industry due to the crucial role of MoS_2 in the catalytic hydrotreatment aimed at the removal of sulfur, nitrogen, oxygen, and metals from oil fractions [9–12].

Molybdenum also exhibits a clear-cut tendency to form binuclear and cluster compounds containing both bridging μ_2- or μ_3-sulfur atoms and metal–metal bonds. For compounds with the $\{M_2(\mu\text{-}S)_2(S)_2\}^{2+}$ core, chalcogen transfer and condensation reactions and participation in redox processes were studied [13]. It was shown in recent works that the polynuclear complexes of molybdenum sulfide can serve as efficient and environmentally safe materials for photo- and electrocatalytic hydrogen evolution [14, 15]. The oxycationic group $\{Mo_2O_2S_2\}^{2+}$ is easily accessible and can be isolated as the complexes $Cs_2[Mo_2O_2S_2(C_2H_4)_2(H_2O)_2] \cdot 2H_2O$ and $[Mo_2O_2S_2(HGly)(Gly)_2]$ with chelating ligands [16, 17]. The glycine complex, $[Mo_2O_2S_2(HGly)(Gly)_2]$, was shown to be catalytically active in the reduction of acetylene to ethylene [17]. In addition, the $\{Mo_2O_2S_2\}^{2+}$ group is used as a building block for modification of polyoxometalate structures in order to combine the properties of various types of compounds at the molecular level, e.g., the electrocatalytic functions of metal sulfide complexes and considerable electron capacity of polyoxymetallates. The resulting hybrid systems based on the chemical and structural complementarity between the initial fragments comprise several tens of metal atoms up to the formation of nano-sized systems and have diverse structural motifs [18].

This communication reports the preparation and characterization of a new oxothiomolybdenum chloride complex, $Cs_3[Mo_2O_2(\mu\text{-}S)_2Cl_4(H_2O)_2]Cl$ (**II**). This is the first example of a binuclear complex with the $\{Mo_2O_2S_2\}^{2+}$ core devoid of chelating ligands and it can serve as a convenient starting compound for the synthesis of other derivatives with the same $\{Mo_2O_2S_2\}^{2+}$ core.

EXPERIMENTAL

The complex $K_2I_2[Mo_{10}O_{10}S_{10}(OH)_{10}(H_2O)_5] \cdot 20H_2O$ (**I**) was prepared by a reported procedure [19]. Other reagents were obtained from commercial sources and used as received.

Synthesis of II. A suspension of **I** (0.50 g, 0.21 mmol) in 15 mL of water was prepared with vigorous stirring, the pH was adjusted to 0.5 by dropwise addition of 12 M hydrochloric acid. The orange reaction mixture was stirred at 40°C for 30 min to increase the solubility of the starting decamolybdate. The resulting orange solution with a minor quantity of a yellow precipitate was cooled to room temperature and filtered. The addition of CsCl (2.53 g, 15 mmol) caused a slight clouding of the reaction mixture. The

Table 1. Crystallographic characteristics and X-ray experiment details for compound **II***

Parameter	Value
Molecular formula	$H_4Cl_5O_4S_2Mo_2Cs_3$
M	900.01
System, space group	Monoclinic; $P2_1/c$
a, Å	14.0306(5)
b, Å	6.9136(3)
c, Å	17.5668(7)
β, deg	91.248(1)
V, $Å^3$	1703.61(12)
Z	4
F(000)	1608
μ, mm^{-1}	8.81
Crystal size, mm	0.10 × 0.02 × 0.02
Absorption correction	Multi-scan SADABS (Bruker-AXS, 2004)
T_{min}, T_{max}	0.473, 0.844
The number of measured/independent/observed ($I > 2\sigma(I)$) reflections	15772/3911/3264
R_{int}	0.041
Data collection range on θ, deg	1.5–27.5
Ranges of reflection indices	$-17 \leq h \leq 18$, $-8 \leq k \leq 8$, $-22 \leq l \leq 22$
$R(F^2 > 2\sigma(F^2))$, $wR(F^2)$; S	0.025, 0.052
GOOF	1.03
The number of independent reflections/refined parameters/constrains	3911/145/0
Weighing scheme	$w = 1/[\sigma^2(F_o^2) + (0.0205P)^2]$, $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$, $e\,Å^{-3}$	1.17, −0.79

* Software used: APEX2 (Bruker-AXS, 2004), SAINT (Bruker-AXS, 2004), SHELXS-97 (Sheldrick, 1998), SHELXL-97 (Sheldrick, 1998), SHELXTL (Bruker-AXS, 2004), and CIFTAB-97 (Sheldrick, 1998).

solution was stirred at room temperature for 1 h and filtered once again. Slow evaporation of the filtrate during a week gave yellow crystals of complex **II**. The product was filtered off on a glass porous filter and washed successively with methanol and diethyl ether. The product yield was 0.42 g (45% in relation to Mo).

X-ray diffraction study of complex II was performed by a standard procedure on a Bruker-Apex DUO automated four-circle diffractometer equipped with a CCD array detector at 150 K (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The reflection intensities were measured using φ and ω scan modes for narrow (0.5°) frames to $2\theta = 55°$. The absorption corrections were applied empirically by the SADABS program [20]. The structure was solved by the direct method and refined by full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms using the SHELXTL program package [21]. The O(1*w*) position is partially occupied by water molecule and chloride anion in 0.9/0.1 ratio, and the Mo(1)–O(1*w*) bond length is 2.448(3) Å. The presence of this statistics gives rise to a similar disorder in the position of Cl(5), which is not coordinated to any molybdenum atom (O(1*w*)–Cl(5), 3.137(2) Å), the Cl^- 0.9/0.1 to H_2O ratio being 0.9 to 0.1 The individual coordinates or thermal parameters of the oxygen and chlorine atoms cannot be determined by separate refinement of these atoms in these positions. Therefore, each position was refined as a (O/Cl) pair with the same coordinates and thermal parameters. The crystallographic characteristics of complex **I** are summarized in Table 1; selected bond lengths and bond angles are in Table 2. The CIF file with full structural information for **II** is deposited at the Fachinformationszentrum Karlsruhe (CSD no. 425748; crysdata@fiz-karlsruhe.de).

RESULTS AND DISCUSSION

Acidification of aqueous solutions of cyclic hydroxyoxothiomolybdates such as $[Mo_{10}O_{10}S_{10}(OH)_{10}(H_2O)_5]$ induces destruction of the hydroxy and aqua bridges [19] giving the aqua ions $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$. These cations may again form cyclic compounds as pH is increased [22] or can be used as building blocks in reactions with

Table 2. Selected bond lengths (Å) and bond angles (deg) in structure **II**

Bond	*d*, Å	Bond	*d*, Å
Mo(1)–S(1)	2.3244(12)	Mo(2)–O(2*w*)	2.316(3)
Mo(1)–S(2)	2.3223(12)	Mo(2)–O(2M)	1.698(3)
Mo(2)–S(1)	2.3102(11)	Mo(1)–Cl(1)	2.4574(12)
Mo(2)–S(2)	2.3150(12)	Mo(1)–Cl(3)	2.5115(11)
Mo(1)–Mo(2)	2.8411(6)	Mo(2)–Cl(2)	2.5285(11)
Mo(1)–O(1*w*)	2.448(3)	Mo(2)–Cl(4)	2.5403(12)
Mo(1)–O(1M)	1.673(3)		
Angle	ω, deg	Angle	ω, deg
S(1)Mo(1)O(1*w*)	85.08(8)	O(1*w*)Mo(1)Cl(1)	75.84(8)
S(2)Mo(1)O(1*w*)	83.61(8)	O(1*w*)Mo(1)Cl(3)	77.98(8)
O(1M)Mo(1)S(1)	101.73(12)	O(1M)Mo(1)Cl(1)	96.08(12)
O(1M)Mo(1)S(2)	101.87(11)	O(1M)Mo(1)Cl(3)	95.41(11)
S(1)Mo(2)O(2*w*)	85.98(8)	O(2*w*)Mo(2)Cl(2)	75.96(8)
S(2)Mo(2)O(2*w*)	86.70(8)	O(2*w*)Mo(2)Cl(4)	78.06(8)
O(2M)Mo(2)S(1)	103.31(11)	O(2M)Mo(2)Cl(2)	92.64(11)
O(2M)Mo(2)S(2)	102.94(12)	O(2M)Mo(2)Cl(4)	90.59(11)

polyoxometalates [18]. The binuclear anionic complex $[Mo_2O_2(\mu\text{-}S)_2Cl_4(H_2O)_2]^{2-}$ (Fig. 1) was isolated upon the reaction of a solution of the decamolybdate acidified with HCl to pH 0.5 with an excess of cesium chloride. Crystallization of the cesium salt **II** starts after several days upon evaporation in an open beaker in air. Yellow needle crystals were isolated after a week and washed with methanol to remove cesium chloride traces.

Complex **II** is the first example of structurally characterized compound with the $\{Mo_2O_2S_2\}^{2+}$ core stabilized without chelating or bridging ligands. The Mo–Mo distance in the anionic part is 2.8411(6) Å, which corresponds to a metal–metal bond. Both molybdenum atoms have a somewhat distorted octahedral environment (without considering the Mo–Mo bond) composed of aqua, oxo, and chloride ligands and two

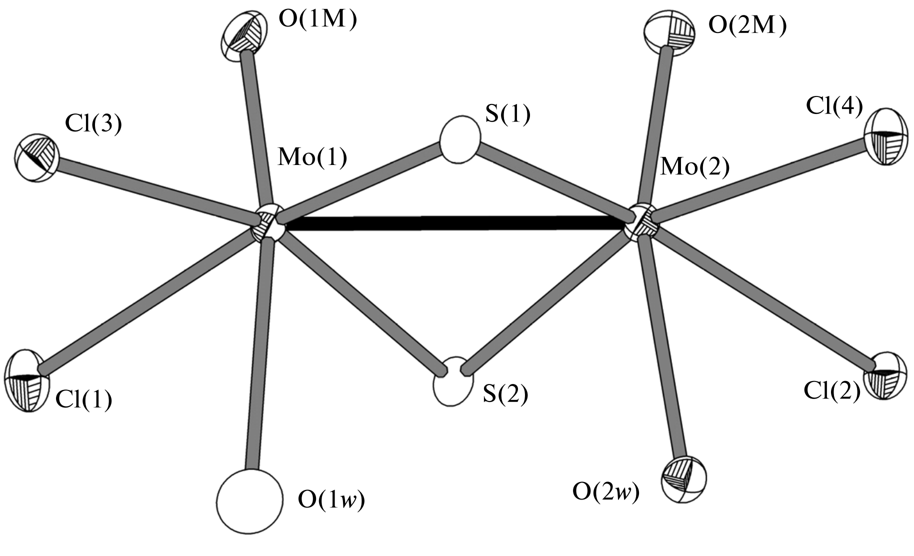

Fig. 1. The $[Mo_2O_2(\mu\text{-}S)_2Cl_4(H_2O)2]^{2-}$ anion in compound **II** (50% probability ellipsoids).

Table 3. Comparison of the geometric parameters of the complexes containing a $\{Mo_2O_2S_2\}^{2+}$ fragment

Parameter (deg, Å)	$Cs_2[Mo_2O_2S_2(C_2H_4)_2(H_2O)_2] \cdot 2H_2O$ [16]	$[Mo_2O_2S_2(HGly)(Gly)_2]$ [17]	**II**
Mo–Mo–O	101.53; 101.42	107.33; 106.54	94.12; 97.41
Mo–Mo=O	99.66; 100.42	82.30; 83.58	95.80; 97.97
Mo–S–Mo	75.35; 74.97	74.63; 74.40	75.57; 75.62
Mo–Mo	2.822(1)	2.816(1)	2.8411(6)
Mo=O	1.691(3); 1.701(3)	1.688(3); 1.681(3)	1.673(3); 1.698(3)
Mo–O	2.165(3), 2.155(3)	2.281(3); 2.322(3)	2.448(3); 2.316(3)
Mo–S	2.308(1)–2.320(1)	2.321(1)–2.332(1)	2.3102(11); 2.3244(12)

sulfide bridges ($(Mo-S)_{av}$ 2.3180(12) Å). The O(1*w*) position coordinated to Mo(1) (2.448(3) Å) (Fig. 1) is partially occupied by a water molecule and a chloride anion in 0.9/0.1 ratio. This means that the crystal structure of **II** comprises two types of anionic complexes, $[Mo_2O_2(\mu\text{-}S)_2Cl_4(H_2O)_2]^{2-}$ (90%) and $[Mo_2O_2(\mu\text{-}S)_2Cl_5(H_2O)]^{3-}$ (10%). This statistical disorder between H_2O and Cl is typical of triangular molybdenum and tungsten sulfide aqua chloro complexes [23].

It is noteworthy that $\{Mo_2O_2(\mu\text{-}S)_2\}^{2+}$ is sufficiently non-rigid and can adjust its geometry to coordinate various ligands. Table 3 compares some geometric parameters of **II** and the previously described compounds with the same core [16, 17]. Oxalate ligands are coordinated to Mo=O according to the *cis–cis* pattern [16], the Mo–Mo–O and Mo–Mo=O angles being opened compared with the geometry of complex **II**. The coordination of the glycine ligand in the *cis–cis* mode also results in an increase in the Mo–Mo–O angles; however, the Mo–Mo=O angles, conversely, decrease [17]. The Mo–Mo distance in **II** is somewhat longer than in the oxalate glycine complexes. The Mo=O and Mo–S bond lengths and the Mo–S–Mo bond angles virtually do not change, which attests to insignificant influence of the outer ligands on the geometry of these bonds. No other chloride complexes with the $\{Mo_2O_2(\mu\text{-}S)_2\}^{2+}$ core

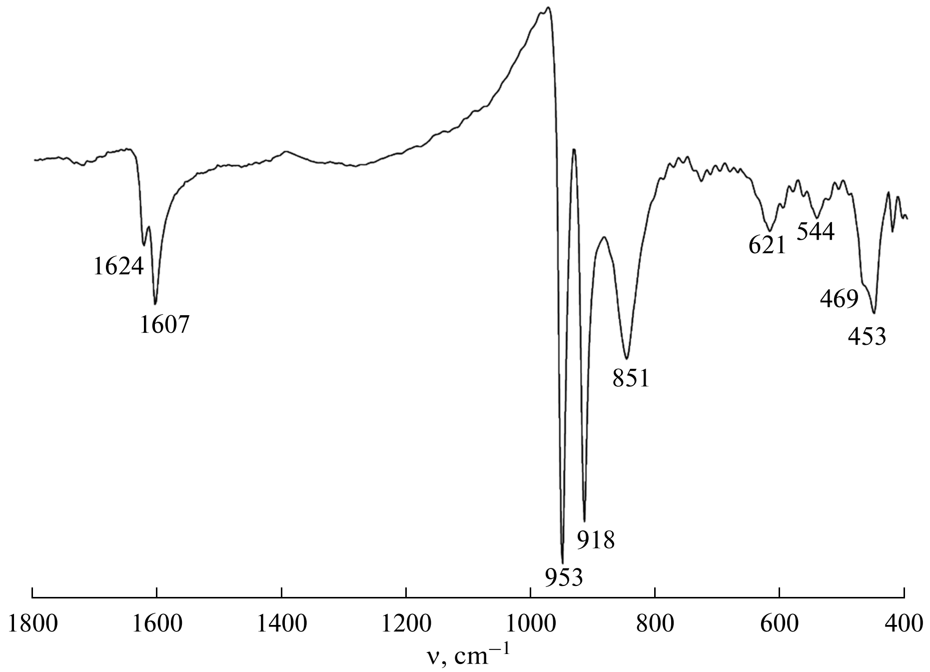

Fig. 2. IR spectrum of complex **II** in the 1800–400 cm^{-1} range.

were reported in the literature; however, the compound $(AsPh_4)_2[W_2O_2(\mu\text{-}S)_2Cl_4]$ (**III**) was described [24]. In this structure, the W–W bond length (2.844(1) Å) almost coincides with the Mo–Mo bond length in **II**. The W–S bond lengths (2.274(5)–2.324(4) Å) and the WSW angles (76.4(1)°) in **III** also do not differ significantly from the corresponding parameters of complex **II**.

The IR spectrum of **II** (Fig. 2) shows two bands, 3402 and 3240 cm^{-1}, in the high-frequency region which are caused by stretching vibrations of water molecules [25]. Figure 2 shows the frequency range from 1800 to 400 cm^{-1}. The 1624 and 1607 cm^{-1} bands are due to the bending vibrations of water molecules [25]. Two bands at 953 and 918 cm^{-1} correspond to symmetric and antisymmetric Mo=O modes, respectively [26]. Three broadened signals at 851, 621, and 544 cm^{-1} refer to the wagging, torsional, and rocking vibration modes of coordinated water molecules [25]. The low-frequency bands at 469 and 453 cm^{-1} are due to the symmetric and antisymmetric Mo–S modes [26, 27].

ACKNOWLEDGMENTS

This study was supported by the Ministry of Education and Science of the Russian Federation, Agreement no. 14.B37.21.1185 “Spherical Keplerate Capsules as Supramolecular Nanoreactors for Organization of Synthetic and Catalytic Processes.” This work was supported by Russian Federation President grant (MK-4318.2013.3).

REFERENCES

1. Stiefel, E.I., *Prog. Inorg. Chem.*, 1977, vol. 22, p. 1.
2. Haber, J., *Bulletin of Climax Molybdenum*, London: Greenwich (CT, USA), 1981.
3. Holm, R.H., *Chem. Soc. Rev.*, 1981, vol. 10, no. 4, p. 455.
4. Coucouvanis, D., *Acc. Chem. Res.*, 1981, vol. 14, no. 7, p. 201.
5. Müller, A., Diemann, E., Jostes, R., and Bögge, H., *Angew. Chem., Int. Ed. Engl.,* 1981, vol. 20, no. 11, p. 934.
6. Müller, A., Jaegermann, W., and Enemark, J.H., *Coord. Chem. Rev.*, 1982, vol. 46, p. 245.
7. Müller, A., *Polyhedron*, 1986, vol. 5, nos. 1–2, p. 323.
8. Rakowsky DuBois, M., *Chem. Rev.*, 1989, vol. 89, p. 1.
9. Eltzner, W., Breysse, M., Lacroix, M., and Vrinat, M., *Polyhedron*, 1986, vol. 5, nos. 1–2, p. 203.
10. Casewit, C.J. and Rakowsky-DuBois, M., *Inorg. Chem.*, 1986, vol. 25, no. 1, p. 74.
11. Weberg, R.T., Haltiwanger, R.C., Laurie, J.C., and Rakowsky DuBois, M., *J. Am. Chem. Soc.*, 1986, vol. 108, no. 20, p. 6242.
12. Müller, A., Diemann, E., Branding, A., et al., *Appl. Catal.*, 1990, vol. 62, no. 1, p. L13.
13. Bhattacharyya, R., Chakrabarty, P.K., Ghosh, P.N., et al., *Inorg. Chem.*, 1991, vol. 30, no. 20, p. 3948.
14. Hou, Y., Abrams, B.L., Vesborg, P.C.K., et al., *Nat. Mater.*, 2011, vol. 10, no. 6, p. 434.
15. Laursen, A.B., Kegnaes, S., Dahl, S., and Chorkendorff, I., *Energy Environ. Sci.*, 2012, vol. 5, no. 2, p. 5577.
16. McDonald, W.S., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1978, vol. 34, no. 9, p. 2850.
17. Wu, J.-F., Li, D.-M., Cui, L.-F., et al., *Appl. Organomet. Chem.*, 2007, vol. 21, no. 12, p. 1033.
18. Cadot, E., Sokolov, M.N., Fedin, V.P., et al., *Chem. Soc. Rev.*, 2012, vol. 41, no. 22, p. 7335.
19. Cadot, E., Salignac, B., Halut, S., and Sécheresse, F., *Angew. Chem., Int. Ed. Engl.*, 1998, vol. 37, no. 5, p. 611.
20. Sheldrick, G.M., *SADABAS. Program for Empirical X-ray Absorption Correction*, Bruker AXS, 1990–2007.
21. Sheldrick, G.M., *SHELXTL. Programs for Structure Solution and Refinement*, Bruker AXS, 1990–2007.
22. Lemonnier, J.-F., Duval, S., Floquet, S., and Cadot, E., *Isr. J. Chem.*, 2011, vol. 51, no. 2, p. 290.
23. Abramov, P.A., Adonin, S.A., Peresypkina, E.V., et al., *J. Struct. Chem.*, 2010, vol. 51, no. 4, p. 731.
24. Drew, M.G.B., Page, E.M., and Rice, D.A., *Inorg. Chim. Acta Lett.*, 1983, vol. 76, no. 1, p. L33.
25. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Hoboken (New Jersey, USA): Wiley, 2009.
26. Coucouvanis, D., *Adv. Inorg. Chem.*, 1998, vol. 45, p. 1.
27. du Peloux, C., Dolbecq, A., Cadot, E., et al., *J. Mol. Struct.*, 2003, vol. 656, nos. 1–3, p. 37.

Translated by Z. Svitanko