

## Accepted Manuscript

Note

Synthesis, characterization and structural analysis of isostructural dinuclear molybdenum and tungsten oxo-bis- $\mu$ -sulfido-benzenedithiolene complexes

Alexander Doering, Carola Schulzke, Qingwei Zhang

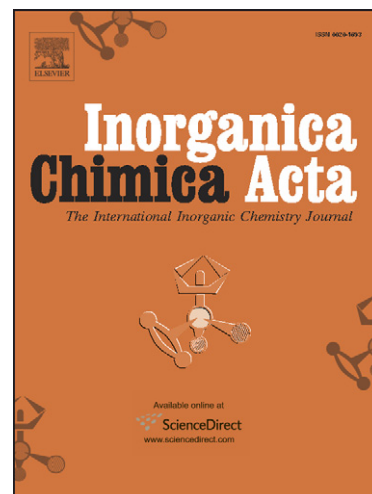
PII: S0020-1693(10)00344-0  
DOI: [10.1016/j.ica.2010.05.036](https://doi.org/10.1016/j.ica.2010.05.036)  
Reference: ICA 13521

To appear in: *Inorganica Chimica Acta*

Received Date: 11 May 2010  
Accepted Date: 18 May 2010

Please cite this article as: A. Doering, C. Schulzke, Q. Zhang, Synthesis, characterization and structural analysis of isostructural dinuclear molybdenum and tungsten oxo-bis- $\mu$ -sulfido-benzenedithiolene complexes, *Inorganica Chimica Acta* (2010), doi: [10.1016/j.ica.2010.05.036](https://doi.org/10.1016/j.ica.2010.05.036)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



**Synthesis, characterization and structural analysis of isostructural dinuclear molybdenum and tungsten oxo-bis- $\mu$ -sulfido-benzenedithiolene complexes**

(NOTE)

Alexander Doering<sup>a)</sup>, Carola Schulzke<sup>b)\*</sup>, Qingwei Zhang<sup>c)</sup>

- a) Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstr. 4, 37077 Göttingen, Germany;
- b) School of Chemistry, Trinity College Dublin, Dublin 2, Ireland; email: [schulzkc@tcd.ie](mailto:schulzkc@tcd.ie), Tel.: ++353-1-8963501;
- c) College of Medicine, Drexel University, Philadelphia, PA 19102, USA;

**Abstract**

Reactions of the molybdenum and tungsten precursors  $[\text{MO}_2\text{S}_2]^{2-}$  with equimolar amounts of benzenedithiol in acetonitrile give the title compounds  $[\text{M}_2\text{O}_2(\mu\text{-S})_2(\text{bdt})_2]^{2-}$  with  $\text{M} = \text{Mo}, \text{W}$  and  $\text{bdt} = \text{benzene-dithiolate}$ . In case a tungsten to ligand ratio of 1:2 is used the dimer forms as well but only as a minor species whereas the monomer  $[\text{WO}(\text{bdt})_2]^{2-}$  is the main product. In both dimeric compounds the *syn*-isomers are formed referring to the position of the apical oxo ligands with respect to the  $\text{M}_2\text{S}_2$  plane. For the molybdenum compound this contrasts with a published crystal structure of the *anti*-isomer. Both complexes give highly symmetric isomorphous crystals but still show subtle differences in their bond lengths and angles around the central metal. The X-ray crystal structures of both are analyzed in detail and compared with each other and with the isomeric molybdenum compound. Differences and similarities between tungsten and both isomers of molybdenum complexes are shown to be more influenced by the conformation than by the central metal and a reason for the formation of *syn*- and *anti*-isomers based on the respective synthetic procedures is proposed.

**Keywords**

molybdenum, tungsten, X -ray crystal structures, isomorphism, *syn/anti* isomerism

**1. Introduction**

Molybdenum and tungsten are chemically very similar because they belong to the same group of the periodic table and are of almost identical size since tungsten's orbitals are contracted by the relativistic effect despite it having 32 electrons more.[1,2,3] Accordingly there are quite a number of analogous complexes of molybdenum and tungsten described in the literature in particular those with oxo ligands like  $[\text{MOCl}_4]$ ,[4]  $[\text{MO}_2\text{Cl}_2]$ ,[5]  $[\text{MOSCl}_2]$ ,[6]  $[\text{MO}(\text{SR})_4]$ [7] and  $[\text{MO}(\text{mnt})_2]^{2-}$  (with *mnt* = maleonitrile<sup>2-</sup>)[8] that are almost identical in many aspects. Contrary to this there are also many examples known for a divergent behavior of molybdenum and tungsten in complex chemistry or biological inorganic chemistry.

Molybdenum and tungsten are used in ubiquitous molybdopterin dependent enzymes in a similar way for similar reactions but in different habitats (usually molybdenum is used at mesophilic conditions and tungsten at thermophilic conditions).[9] Furthermore, a tungsten specific biological transporter in *Pyrococcus furiosus* is able to distinguish between molybdate and tungstate though it is not clear yet how it does this.[10]

A distinct behavior of both metals has also been reported frequently in a chemical context: a simple homoleptic chloro complex in oxidation state six is only stable with tungsten as central metal but not with molybdenum.[11] and in order to prepare the di-oxo bis-acetylacetonato complexes  $[\text{MO}_2(\text{acac})_2]$  two different methods need to be employed for both metals.[12] Similarly, though both  $[\text{MOCl}_4]$  compounds are accessible, the most convenient synthetic procedure for tungsten does not work for molybdenum.[4,5] In another case identical synthetic procedures lead to quite different products for analogous molybdenum and tungsten precursors.[13]

Therefore generally there are numerous examples for both a congruent and a distinct behavior of molybdenum and tungsten *in vivo* and *in vitro*. Comparing synthetic molybdenum and

tungsten compounds that are either analogous or behave differently in reactions is therefore still of great importance for understanding the subtle differences that are fundamental for the biological relevance and the distinct chemical character of both metals.

## 2. Results and Discussion

### *Synthesis and structural analysis*

$[\text{W}_2\text{O}_2(\mu\text{S})_2(\text{bdt})_2]^{2-}$  (**1**) was initially obtained as byproduct in the preparation of  $[\text{WO}(\text{bdt})_2]^{2-}$  from  $[\text{WO}_2\text{S}_2]^{2-}$  and  $\text{H}_2\text{bdt}$  (see scheme 1). The central  $\text{M}_2\text{O}_2\text{S}_2$  moiety of this compound is a long and very well known, often observed motif in molybdenum chemistry [14] but not as common in tungsten chemistry where only a few examples of small molecule structures have been reported [14f, 15]. In addition its *syn* conformation with respect to the axial oxo-ligands' position relative to the  $\text{W}_2\text{S}_2$ -plane was in contrast to the published structure of its molybdenum analog [14a]. Consequently the synthetic procedure was modified to obtain the dimeric compound as only or major product and successfully applied to both the respective tungsten and molybdenum precursors.

With these two compounds we are now able to shed light on the reason for the preference of forming *syn*- or *anti*-isomers, to provide a further example for an analogous behavior of molybdenum and tungsten in synthesis and to compare the respective compounds structurally. The dimeric tungsten (**1**) and molybdenum (**2**) complexes were obtained in moderate and low yield respectively and characterized by IR spectroscopy, Mass spectrometry (in which the molecular peaks were directly observed), elemental analysis and X-ray structural analysis (Fig. 1). Both compounds give isomorphous structures in the orthorhombic space group *Pbca* with the complexes in their *syn* conformation, which for the molybdenum compound is contrary to the previously published structure.

A structural comparison of these two compounds and of the known molybdenum *anti*-isomer (table 1) shows that almost all structural parameters are more strongly influenced by the conformation of the molecule than by the nature of the two central metals. This is most evident in

the metal metal distances being longest for the molybdenum *anti*-isomer (2.9018 Å vs. 2.8905 Å for Mo<sub>syn</sub> and 2.8797 Å for W) and the metal's distance from the plane formed by the four sulfur atoms (of one dithiolene ligand and the two bridging sulfides) which is significantly shorter for the molybdenum *anti*-isomer (0.62 Å vs. 0.71 Å for Mo *syn* and 0.69 Å for W *syn*). Furthermore the angle between one bridging sulfide and the dithiolene sulfur *trans* to it is significantly larger for the molybdenum *anti*-isomer (147.22° vs. 143.57° for Mo<sub>syn</sub> and 144.29° for W respectively).

**Table 1:** Bond distances (in Å) and angles (in °) for **1**, **2** and the *anti*-isomer of **2**[14a]

	W (1)		Mo ( <i>syn</i> ) (2)		Mo ( <i>anti</i> )[14a]
M-M	2.8797(3)		2.8905(4)		2.9018(13)
M=O	1.697(4)	W1	1.699(2)	Mo1	
	1.708(4)	W2	1.784(2)	Mo2	
average	1.7025		1.7415		1.697
M-μS	2.3351(15)	W1	2.3314(9)	Mo1	
	2.3381(15)	W1	2.3332(9)	Mo1	
	2.3410(16)	W2	2.3344(9)	Mo2	
	2.3457(15)	W2	2.3395(9)	Mo2	
average	2.3400		2.3346		2.3075
M-S(bdt)	2.4024(16)	W1	2.4050(8)	Mo1	
	2.4183(15)	W1	2.4220(8)	Mo1	
	2.4057(15)	W2	2.4059(9)	Mo2	
	2.4119(14)	W2	2.4129(8)	Mo2	
average	2.4096		2.411		2.485
M-(S4-plane)	0.6883	W1	0.7060	Mo1	
	0.6996	W2	0.7143	Mo2	
average	0.6940		0.7102		0.6242
μS-M-μS	101.50(5)	W1	100.68	Mo1	
	101.10(5)	W2	100.40	Mo2	
average	101.30		100.54		102.10
S-M-S	81.32(5)	W1	81.29	Mo1	
	81.68(5)	W2	81.57	Mo2	
average	81.50		81.43		81.02
μS-M-S(cis)	78.95(5)	W1	78.85	Mo1	
	78.61(5)	W1	78.55	Mo1	
	78.29(5)	W2	78.32	Mo2	
	78.66(5)	W2	78.52	Mo2	
average	78.63		78.56		80.23
μS-M-S(trans)	146.29(6)	W1	145.81	Mo1	
	142.66(6)	W1	141.63	Mo1	
	143.76(6)	W2	143.21	Mo2	
	144.44(6)	W2	143.64	Mo2	

average	144.29		143.57		147.22
---------	--------	--	--------	--	--------

Overall the *anti* conformation allows the metal to be in a less distorted square planar coordination geometry (being closer to the base of the square pyramid) compared with the *syn* conformation. Notably, with respect to both latter features the tungsten complex (and not the molybdenum *syn*-isomer) is the one with structural properties more similar to the molybdenum *anti*-isomer. In addition these are the properties that show the most pronounced differences between molybdenum and its tungsten analog aside from the average metal-oxo distance. The latter, however, is in case of the molybdenum complex not reliable due to a disorder of one of the oxo ligands (O2) with an abnormal large distance to molybdenum. Interestingly this distance is in a range that has been observed in protein X-ray absorption spectroscopy leading to the ambiguous assignment of the respective ligand as an oxo ligand or a hydroxide.[16] In case of the present small molecule structure, however, a coordinated hydroxide can clearly be excluded due to the presence of two cations and the fact that the complex is diamagnetic. In addition, no  $^1\text{H-NMR}$  signal was observed that could be assigned to an  $\text{OH}^-$  proton.

In both *syn*-isomers the metal sulfide distances are longer for tungsten than for molybdenum, which is surprising considering that usually tungsten is the more thiophilic metal of both. For the metal dithiolene sulfur distances this order is reversed and therefore as expected. All metal sulfur distances are, however, only marginally distinct, with differences being close to the experimental error.

Despite this distinction in summary the metals influence on structural parameters is indeed considerably smaller than that of the conformation.

#### *Syn and anti conformation*

In a recent theoretical study about the *syn/anti* isomerism of compounds with the  $\text{M}_2\text{O}_2\text{S}_2$  moiety it was found that the *syn*-isomer is thermodynamically favored but only by about 1 – 4 Kcal  $\text{mol}^{-1}$  which was ascribed to the  $\sigma$  interaction of the two metals based on the relative orientation of

their respective d orbitals being bent in the *syn*-isomer but lateral in the *anti*-isomer.[17] This is in accordance with the structural parameters discussed above. In order to achieve a better orbital overlap for the bent metal-metal interaction the metals are forced above the S4 plane to a larger extent in the *syn*-isomers. For molybdenum this feature is even a bit more pronounced than for tungsten because the latter is slightly more flexible with respect to orbital shape and orientation.

The authors of the theoretical study[17] further suggest that it is mainly the nature and location of the cation in the crystal structure that dictates the conformation of the complex. Chemically this is very unlikely because an exchange of cation would certainly not be able to form one isomer out of the other which would require a disconnection of at least two metal-sulfur bonds and a 180° turn of one of the two fragments. So if the cation had an influence on the formation of only one of the isomers this could only be relevant during the actual reaction leading to the dimer. Furthermore, we have now synthesized the *syn* molybdenum complex **2** as isomer to its *anti* form with the exact same cation, which was already present during dimer formation. We rather propose that it is the nature of the metal precursor that influences which of the two isomers is preferentially synthesized.

In case of the *anti*-isomer the precursor carried already the benzenedithiolene ligand and two of the three oxo ligands were replaced by the then bridging sulfides. Here it is sterically easier for both metal fragments to approach each other with the aromatic rings furthest apart and the two oxo ligands on opposite sides of the product. In case of our *syn*-isomer the metal precursor already contains the  $\text{MOS}_2$  moiety and it is likely that first or simultaneously with the dithiolene coordination the  $\text{M}_2\text{O}_2\text{S}_2$  core was formed by reduction of both metal centers to  $\text{M(V)}$ , oxidation of two sulfide ligands and subsequent elimination of persulfide from the complex. When such small molecule fragments without sterical demand react with each other, the metal-metal interaction becomes more dominating and the *syn*-core that allows a better overlap of the respective orbitals giving rise to the thermodynamic advantage, despite it being very small, is more likely to form.

In conclusion we have prepared and characterized by X-ray crystallography analogous  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{bdt})_2]^{2-}$  and  $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{bdt})_2]^{2-}$  and shown that in this case the conformation has a

stronger influence on structural parameters in the crystal structures than the central metal. Furthermore, we have demonstrated that both the *anti*-[14a] and the *syn*-isomer of  $[\text{NEt}_4]_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{bdt})_2]$  can be prepared and that it is not the cation that dictates the conformation but rather the synthetic procedure with respect to the metal precursor.

### 3. Experimental

#### *General*

The compounds have been synthesized under a pure nitrogen atmosphere using Schlenk line techniques. Solvents were pre-dried two days over KOH and refluxed for three days over calcium hydride, sodium/benzophenone or phosphorus pentoxide before distilled onto freshly regenerated molecular sieves.  $(\text{NEt}_4)_2[\text{MoO}_2\text{S}_2]$ [18] and  $(\text{NEt}_4)_2[\text{WO}_2\text{S}_2]$ [18] have been synthesized according to the respective literature procedures. Other chemicals were purchased commercially and used as received.

#### *Synthesis of $[\text{NEt}_4]_2[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{bdt})_2]$ 1*

Method I: A solution of 0.17 g (1.2 mmol) of benzene-1,2-dithiol in 5 ml acetonitrile was added to a stirred solution of 0.62 g (1.1 mmol) of  $[\text{Et}_4\text{N}]_2[\text{WO}_2\text{S}_2]$  in 20 ml acetonitrile at room temperature. The color of the solution changed from yellow to red-brown immediately. After 2 h, the solution was filtered and the filtrate was dried under vacuum to afford a red-brown solid  $[\text{Et}_4\text{N}]_2[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{bdt})_2]$  (yield: 66 %). IR (KBr) ( $\text{cm}^{-1}$ ): 1550(m), 1478(s), 1457(w), 1441(s), 1420(m), 1391(s), 1284(w), 1240(s), 1171(s), 1102(s), 1052(w), 998(s), 944(vs), 932(s), 904(w), 782(m), 747(s), 664(s), 437(s), 362(s), 335(m); ESI-MS:  $m/z$  (%) 746 (30) ( $\text{M}_a+\text{H}$ )<sup>+</sup>, 604 (33) ( $\text{M}_a\text{-bdt}+\text{H}$ )<sup>+</sup>; *Anal.* *Calc.* for  $\text{C}_{28}\text{H}_{48}\text{N}_2\text{O}_2\text{S}_6\text{W}_2$  (1004.76 g/mol): C, 33.47; H, 4.82; N, 2.79; found: C, 33.56; H, 4.83; N, 2.65.

Method II: A solution of 0.33 g (2.3 mmol) of benzene- 1,2-dithiol in 5 ml acetonitrile was added to a stirred solution of 0.62 g (1.1 mmol) of  $[\text{Et}_4\text{N}]_2[\text{WO}_2\text{S}_2]$  in 20 ml acetonitrile at room temperature.



The color of the solution changed from yellow to red-brown immediately. After 2 h, the solution was filtered. Slow addition of 4 ml diethyl ether by vapor diffusion to this filtrate afforded the monomeric compound as red-brown needle like crystals  $[\text{Et}_4\text{N}]_2[\text{WO}(\text{bdt})_2]$  (yield: 57 %). IR (KBr) ( $\text{cm}^{-1}$ ): 1546(m), 1480(vs), 1457(vs), 1438(vs), 1393(s), 1307(m), 1262(m), 1233(m), 1182(s), 1102(m), 1077(w), 1033(m), 1022(s), 1004(m), 948(m), 902(m), 885(vs), 848(s), 796(s), 752(s), 663(m), 660(m), 614(w), 544(w), 447(vs), 350(w), 319(m); ESI-MS:  $m/z$  (%) 479 (5) ( $M_a + \text{H}$ )<sup>+</sup>, 338 (30) ( $M_a - \text{bdt} + \text{H}$ )<sup>+</sup>; *Anal. Calc.* for  $\text{C}_{28}\text{H}_{48}\text{N}_2\text{OS}_4\text{W}$  (740.79 g/mol): C, 45.40; H, 6.53; N, 3.78; found: C, 43.89; H, 6.43; N, 4.04.

After 10 days at room temperature, the byproduct of  $[\text{NEt}_4]_2[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{bdt})_2]$  was afforded as cubic red-brown crystals (yield: 16 %). IR (KBr) ( $\text{cm}^{-1}$ ): 1550(m), 1478(s), 1457(w), 1441(s), 1420(m), 1391(s), 1284(w), 1240(s), 1171(s), 1102(s), 1052(w), 998(s), 944(vs), 932(s), 904(w), 782(m), 747(s), 664(s), 437(s), 362(s), 335(m); ESI-MS:  $m/z$  (%) 746 (30) ( $M_a + \text{H}$ )<sup>+</sup>, 604 (33) ( $M_a - \text{bdt} + \text{H}$ )<sup>+</sup>.

#### *Synthesis of $[\text{NEt}_4]_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{bdt})_2]$ **2***

A solution of 1,2-benzenedithiole (0.10 g, 0.70 mmol) in acetonitrile (5 ml) was added slowly to a solution of  $(\text{NEt}_4)_2[\text{MoO}_2\text{S}_2]$  (0.36 g, 0.80 mmol) in 20 ml  $\text{CH}_3\text{CN}$  at room temperature. A color change from orange to red brown was observed. After 2 h stirring at room temperature the solution was filtered and  $\text{Et}_2\text{O}$  (5 ml) was added to the filtered solution. The solution was stored at  $-35^\circ\text{C}$  and after 10 d orange-red crystals were collected. Yield: 0.11 g, 0.13 mmol, 17%

IR (Nujol) ( $\text{cm}^{-1}$ ): 465 (w), 722 (m), 864 (w), 966 (w), 1078 (w), 1170 (w), 1305 (w), 1377 (ws), 1463 (ws), 2301 (s, b), 2345 (s), 2361 (m), 2677 (w), 2775 (w), 2837 (ws), 2857 (m), 2882 (m), 2996 (m), 2923 (s), 2974(ws); MS [FAB<sup>+</sup>, 3-NBA],  $e/z$  (%): 130.2 (100) [ $\text{NEt}_4^+$ ]; MS [FAB<sup>-</sup>, 3-NBA],  $e/z$  (%): 571.5 [ $\text{MoO}_2\text{S}_4(\text{bdt})_2^{2-}$ ]; *Anal. calc.* for  $\text{C}_{28}\text{H}_{48}\text{Mo}_2\text{O}_2\text{S}_6$ : C: 40.57; H: 5.84; N: 3.38; S: 23.21; found: C: 39.84, H: 5.62; N: 3.03; S: 23.05; <sup>1</sup>H-NMR (200 MHz, DMSO- $[\text{d}_6]$ , 25°C, TMS):  $\delta$  = 1.15 (t, 24 H, <sup>3</sup>J = 7.2 Hz,  $\text{CH}_3$ ), 3.18 (q, 16 H, 7.2 Hz,  $\text{CH}_2\text{-CH}_3$ ), 6.76 (m, 4 H,  $\text{H}_{\text{Arom}}$ ), 7.49 (m, 4 H,  $\text{H}_{\text{Arom}}$ ) ppm.

*X-ray Structure Determinations*

The X-Ray crystallographic data of crystals of [NEt<sub>4</sub>]<sub>2</sub>·**1** and [NEt<sub>4</sub>]<sub>2</sub>·**2** were collected on a STOE-IPDS2 with graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. The structures were solved by direct methods (SHELXS-97)[19] and refined with all data by full matrix least squares methods on  $F^2$ . [19] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were attached at idealized positions on carbon atoms and were refined as riding atoms with uniform isotropic thermal parameters. Parameters of the X-ray crystallography are summarized in Table 2. CCDC-760711 (**1**) and CCDC-760712 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 2:** Crystallographic data for the structural analyses of [NEt<sub>4</sub>]<sub>2</sub>[W<sub>2</sub>O<sub>2</sub>( $\mu$ S)<sub>2</sub>(bdt)<sub>2</sub>] and [NEt<sub>4</sub>]<sub>2</sub>[Mo<sub>2</sub>O<sub>2</sub>( $\mu$ S)<sub>2</sub>(bdt)<sub>2</sub>].

	[NEt <sub>4</sub> ] <sub>2</sub> · <b>1</b>	[NEt <sub>4</sub> ] <sub>2</sub> · <b>2</b>
Empirical formula	C <sub>28</sub> H <sub>48</sub> N <sub>2</sub> O <sub>2</sub> S <sub>6</sub> W <sub>2</sub>	C <sub>28</sub> H <sub>48</sub> Mo <sub>2</sub> N <sub>2</sub> O <sub>2</sub> S <sub>6</sub>
CCDC-No.	760711	760712
<i>T</i> [K]	133(2)	133(2)
Crystal system	orthorhombic	orthorhombic
Space group	Pbca	Pbca
<i>a</i> [Å]	12.4588(4)	12.4565(3)
<i>b</i> [Å]	17.3277(7)	17.3548(5)
<i>c</i> [Å]	32.6412(15)	32.7301(7)
<i>V</i> [Å <sup>3</sup> ]	7046.7(5)	7075.6(3)
<i>Z</i>	8	8
<i>D</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.894	1.556
$\mu$ [mm <sup>-1</sup> ]	6.908	1.091
<i>F</i> (000)	3920	3408
$\theta$ range [°]	2.06 to 24.90	1.24 to 25.63
Data/restraints/parameters	6122 / 0 / 369	6653 / 0 / 372
Reflections collected/unique	72404/6122 ( $R_{\text{int}} = 0.1253$ )	55893/6653 ( $R_{\text{int}} = 0.0971$ )

R1, wR2 [I > 2σ(I)] [a]	0.0284, 0.0530	0.0361, 0.0792
R1, wR2 (all data) [a]	0.0515, 0.0568	0.0449, 0.0827
GoF	0.863	1.077
Δρ(max), Δρ(min) [e Å <sup>-3</sup> ]	0.687, -1.420	0.860, -0.757

$$[a] R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR2 = [\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}]^{0.5}.$$

### Other Physical Measurements

Elemental analyses were performed with a Heraeus CHN-O-Rapid elemental analyzer. Infrared spectra were recorded as KBr pellets with a Bio-Rad Digilab FTS-7 spectrometer from 4000 to 300 cm<sup>-1</sup>. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. <sup>1</sup>H- NMR spectra were recorded on a Bruker Avance DRX 200 MHz instrument and referenced to the deuterated solvent.

### Acknowledgements

Financial support of the DFG (Deutsche Forschungsgemeinschaft) is gratefully acknowledged.

### References

- [1] P. Pyykkö, *Chem. Rev.* **88** (1988) 563-594
- [2] A. L. Tenderholt, R. K. Szilagyi, R. H. Holm, K. O. Hodgson, B. Hedman, E. I. Solomon, J. *Inorg. Biochem.* **101** (2007) 1594-1600
- [3] R. D. Shannon, *Acta Cryst. A* **1979**, *32*, 751-767
- [4] J. A. Nielson, *Inorg. Synth.* **1990**, *28*, 323-326
- [5] V. C. Gibson, T. P. Kee, A. Shaw, *Polyhedron* **1988**, *7*, 579-580
- [6] V. C. Gibson, T. P. Kee, A. Shaw, *Polyhedron* **1990**, *9*, 52293-52298
- [7] a) G. R. Hanson, A. A. Brunette, A. C. McDonell, K. S. Murray, A. G. Wedd, *J. Am. Chem. Soc.* **1981**, *103*, 1953-1959; b) I. W. Boyd, I. G. Dance, K. S. Murray, A. G. Webb, *Aust. J. Chem.* **1978**, *31*, 2423-2430; c) I. W. Boyd, I. G. Dance, K. S. Murray, A. G. Webb, *Aust. J. Chem.* **1978**, *31*, 279-

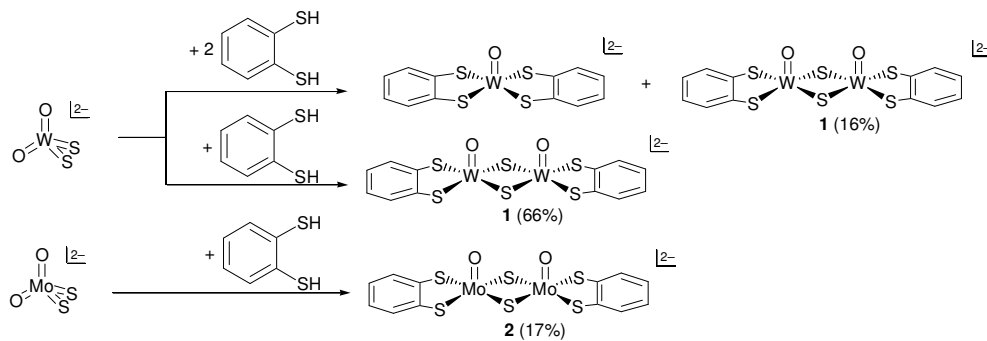
- [8] a) S. K. Das, D. Biswas, R. Maiti, S. Sarkar, *J. Am. Chem. Soc.* **1996**, *118*, 1387-1397; b) S. K. Das, P. K. Chaudhury, D. Biswas, S. Sarkar, *J. Am. Chem. Soc.* **1994**, *116*, 9061-9070
- [9] a) R. Hille, *Chem. Rev.* **1996**, *96*, 2757-2816; b) M. K. Johnson, D. C. Rees, M. W. W. Adams, *Chem. Rev.* **1996**, *96*, 2817-2839; c) C. Kisker, H. Schindelin, D. Baas, J. Rétey, R. U. Meckenstock, P. M. H. Kroneck, *FEMS Microbio. Rev.* **1999**, *22*, 502-521; d) L. E. Bevers, P.-L. Hagedoorn, W. R. Hagen, *Coord. Chem. Rev.* **2009**, *253*, 269-290
- [10] L. E. Bevers, P.-L. Hagedoorn, G. C. Krijger, W. R. Hagen, *J. Bacteriol.* 2006, **188**, 6498-6505
- [11] G. A. Heath, K. A. Mook, D. W. A. Sharp, L. J. Yellowlees, *J. Chem. Soc., Chem. Commun.* **1985**, 1503-1505
- [12] a) G.J.-J. Chen, J. W. McDonald, W. E. Newton, *Inorg. Chem.* **1976**, *15*, 2612-2615; b) C. A. Rice, P. M. H. Kroneck, J. T. Spence, *Inorg. Chem.* **1981**, *20*, 1996-2000
- [13] Q. Zhang, K. Starke, C. Schulzke, A. Hofmeister, J. Magull, *Inorg. Chim. Acta* **2007**, *360*, 3400-3407
- [14] a) J.-J. Wang, S. Groysman, S. C. Lee, R. H. Holm, *J. Am. Chem. Soc.* **2007**, *129*, 7512-7513; b) R. Dessapt, C. Simonnet-Jégat, A. Mallard, H. Lavanant, J. Marrot, F. Sécheresse, *Inorg. Chem.* **2003**, *42*, 6425-6431; c) D. Coucouvanis, A. Iladjikyriacou, A. Toupadakis, S.-M. Koo, O. Ileperuma, M. Draganjac, A. Salifoglou, *Inorg. Chem.* **1991**, *30*, 754-767; d) D. Coucouvanis, *Adv. Inorg. Chem.* **1997**, *45*, 1-7; e) J. I. Gelder, J. H. Enemark, *Inorg. Chem.* **1977**, *15*, 1839-1843; f) R. Llusar, S. Triguero, C. Vicent, M. N. Sokolov, B. Domercq, M. Fourmigue, *Inorg. Chem.* **2005**, *44*, 8937-8946; g) B. Spivack, Z. Dori, *Coord. Chem. Rev.* **1975**, *17*, 99-136 and literature cited therein
- [15] a) D. Rehder, W. Zhang, X. Wu, M. Ebel, C. Bader, *Inorg. Chim. Acta* **2005**, *358*, 1981-1986; b) M. Yamasaki, T. Shibahara, *Inorg. Chim. Acta* **1993**, *205*, 45-51; c) A. Müller, M. Römer, C. Römer, U. Reinsch-Vogell, H. Bögge, U. Schimanski, *Monatshefte f. Chem.* 1985, *116*, 711-717; d) M. F. Mackay, P. J. Oliver, C. G. Young, *Aust. J. Chem.* **1989**, *42*, 837-843
- [16] a) T. Conrads, C. Hemann, G. N. George, I. J. Pickering, R. C. Prince, R. Hille, *J. Am. Chem. Soc.* **2002**, *124*, 11276-11277; b) M. J. Maher, J. Santini, I. J. Pickering, R. C. Prince, J. M. Macy, G. N. George, *Inorg. Chem.* **2004**, *43*, 402-404

[17] M.-M. Rohmer, M. Bénard, *C. R. Chimie* **2005**, *8*, 1093-1100

[18] J. W. McDonald, G. D. Friesen, L. D. Rosenhein, W. E. Newton, *Inorg. Chim. Acta* **1983**, *72*, 205-210

[19] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122

Figures



Scheme 1: Synthetic procedures for the preparation of  $[\text{W}_2\text{O}_2(\mu\text{S})_2(\text{bdt})_2]^{2-}$  (**1**) and  $[\text{Mo}_2\text{O}_2(\mu\text{S})_2(\text{bdt})_2]^{2-}$  (**2**) in acetonitrile at RT.

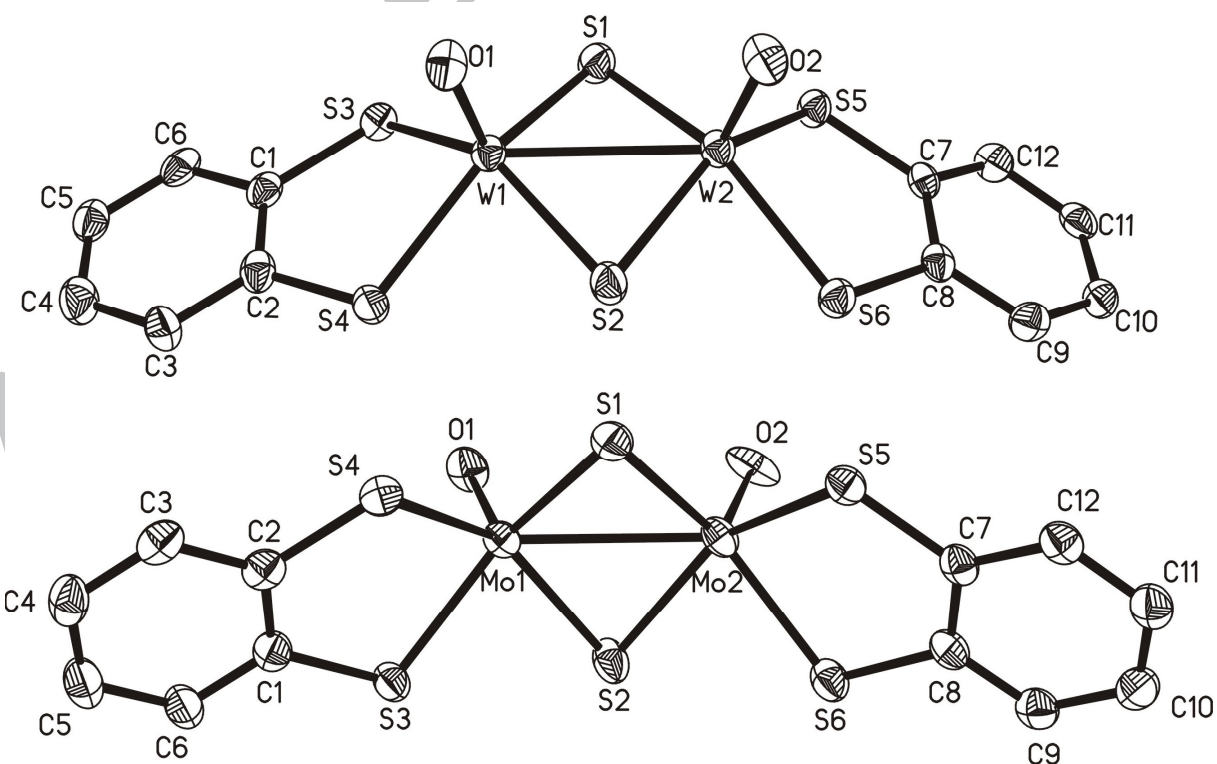


Figure 1: Molecular structures of **1** (top) and **2** (bottom). Thermal ellipsoids are shown at 50% probability. H atoms are omitted for clarity reasons.

*Graphical abstract*

Isostructural dinuclear molybdenum and tungsten oxo-bis- $\mu$ -sulfido-benzenedithiolene complexes have been prepared in *syn*-conformation, characterized crystallographically and compared with each other and the known *anti*-isomer of molybdenum.

