

# Synthesis and X-ray Molecular Structure of $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$ Completing the Structural Characterization of the Series $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{n-}$ ( $n = 0, 1, 2$ ): Trigonal-Prismatic versus Octahedral Coordination in Tris(benzene-1,2-dithiolato) Complexes

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*Dedicated to Prof. Karl Wieghardt on the occasion of his 60th birthday*

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The tris(benzene-1,2-dithiolato) complex  $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  **1** was synthesized from  $[\text{W}(\text{CH}_3)_6]$  and  $\text{C}_6\text{H}_4(\text{SH})_2-1,2$  in diethyl ether. Crystals of  $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  were obtained from a saturated dichloromethane solution at room temper-

ature. The X-ray crystal structure analysis revealed that the tungsten atom in **1** is coordinated in an almost perfect trigonal-prismatic fashion with W–S distances between 2.3724(14) Å and 2.3840(14) Å.

## Introduction

The first molecular trigonal-prismatic tris(dithiolene) metal complex was reported in 1965.<sup>[1]</sup> Ever since, the reasons for the formation of complexes with a trigonal-prismatic coordination geometry over octahedral complexes have been discussed extensively.<sup>[2]</sup> In addition, the “non-innocent” nature of benzenedithiolato ligands and their derivatives has more recently become a field of considerable interest.<sup>[3]</sup> Nevertheless, the trigonal-prismatic coordination geometry is not limited to tris(dithiolene) complexes, but can also be observed for some hexaarylthiolato<sup>[4]</sup> and hexaorgano complexes with six monodentate ligands. The latter complexes have received a great deal of attention since the molecular structure of the complex  $[\text{Li}(\text{tmed})_2][\text{Zr}(\text{CH}_3)_6]$  containing a distorted trigonal-prismatic coordinated zirconium atom was reported.<sup>[5]</sup> Recently,  $[\text{M}(\text{CH}_3)_6]^{2-}$  complexes of Ta ( $z = 1$ ), Nb ( $z = 1$ ), Re ( $z = 0$ ) and W ( $z = 0$ ) have been characterized by X-ray diffraction revealing a regular to slightly distorted trigonal-prismatic coordination geometry.<sup>[6]</sup> Theoretical studies indicate that  $d^0$  ions in particular tend to form complexes with a trigonal-prismatic geometry.<sup>[2c,2d,7]</sup> However, the pseudo-octahedral  $d^0$  complex dianion  $[\text{Zr}^{\text{IV}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{2-}$  is one of the few exceptions to this postulate.<sup>[8]</sup> The coordination geometry in  $[\text{Mo}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  is, as expected, trigonal-prismatic (av-

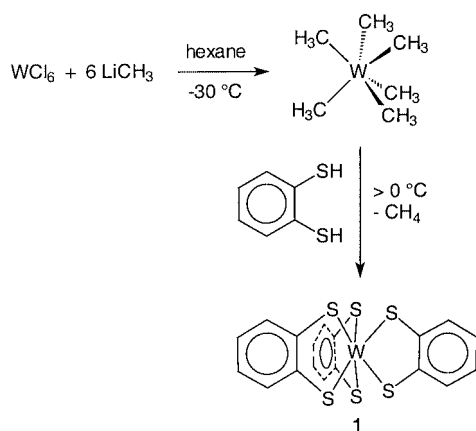
erage twist angle  $0^\circ$ )<sup>[9]</sup> while the geometry of  $[\text{Mo}^{\text{V}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^-$  was found to be closer to octahedral (average twist angle  $33.5^\circ$ )<sup>[10]</sup> than to trigonal-prismatic. Based on this observation a geometry with an even larger twist angle and therefore even closer to octahedral geometry would be expected for the structurally as-yet-uncharacterized  $d^2$  complex  $[\text{Mo}^{\text{IV}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{2-}$ . However, in the homologous series of tungsten complexes the derivative  $[\text{W}^{\text{V}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^-$  exhibits a geometry analogous to the  $\text{Mo}^{\text{V}}$  complex in-between octahedral and trigonal-prismatic (average twist angle  $33^\circ$ )<sup>[11]</sup> while the complex  $[\text{W}^{\text{IV}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{2-}$  is clearly trigonal-prismatic (average twist angle  $3.5^\circ$ )<sup>[12]</sup> It appears that the stepwise reduction of the  $d^0$   $\text{M}^{\text{VI}}$  center does not always enhance the tendency for the formation of octahedral complexes. However, the molecular structure of  $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  has not been described. To compare the molecular structures of the complete series of complexes  $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{n-}$  ( $n = 0, 1, 2$ ) we prepared the missing derivative  $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  and determined its molecular structure by X-ray diffraction.

## Results and Discussion

In connection with our research on helicates with benzene-1,2-dithiolato ligands<sup>[13]</sup> we investigated methods for the preparation of  $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$ . Published syntheses of tris(benzene-1,2-dithiolato) transition metal complexes<sup>[2d]</sup> involve the reaction of metal halides with an excess of benzene-1,2-dithiol in  $\text{CCl}_4$  with liberation of gaseous HCl. The moderate yields as well as the solvent tox-

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icity and the highly reactive by-product in these syntheses proved disadvantageous in our opinion. A rather exotic way to prepare hexakis(arylthiolato) zirconate complexes with six monodentate thiolato ligands using  $[\text{Zr}(\text{CH}_3)_6]^{2-}$  as a precursor was reported by Giolando et al.<sup>[4]</sup> Using this approach, we have improved the synthesis for  $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  (**1**) by reacting  $[\text{W}(\text{CH}_3)_6]$  with three equivalents of benzene-1,2-dithiol in diethyl ether with formation of unreactive methane gas (Scheme 1). The product can be isolated in pure form and in yields of about 70%. The perorgano precursor was prepared in situ from  $\text{WCl}_6$  and  $\text{CH}_3\text{Li}$  in diethyl ether similar to a literature method.<sup>[14]</sup> Bright purple, air-stable crystals of **1** can be obtained from a saturated turquoise dichloromethane solution at ambient temperature.



Scheme 1. Preparation of  $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  from  $[\text{W}(\text{CH}_3)_6]$

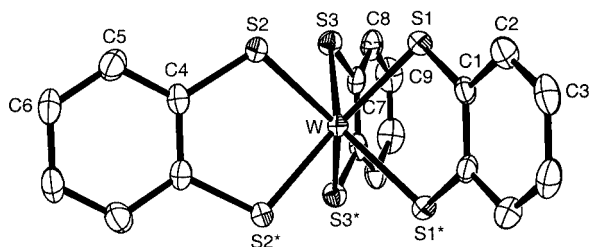


Figure 1. Molecular structure of  $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  (**1**) with the crystallographic numbering scheme; hydrogen atoms have been omitted; starred atoms are related to their corresponding atoms by a crystallographic mirror plane; selected bond lengths [Å] and angles [°]: W–S1 2.3840(14), W–S2 2.3836(13), W–S3 2.3724(14), S1–C1 1.743(5), S2–C4 1.747(5), S3–C7 1.742(6); S1–W–S1\* 81.97(7), S1–W–S2 80.89(5), S1–W–S2\* 134.42(5), S1–W–S3 81.96(5), S1–W–S3\* 136.33(5), S2–W–S2\* 81.73(6), S2–W–S3 82.02(5), S2–W–S3\* 136.24(5), S3–W–S3\* 82.30(7), C1–S1–W 103.21(17), C4–S2–W 107.92(18), C7–S3–W 106.17(19)

Figure 1 shows the molecular structure of the neutral complex **1** along with the crystallographic numbering scheme. The molecular geometry of complex **1** is remarkably similar to its lower homologue  $[\text{Mo}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$ .<sup>[9]</sup> The tungsten(vi) ion is coordinated by six sulfur atoms of three benzene-1,2-dithiolato ligands in an almost perfect trigonal-prismatic fashion with a crystallographically imposed twist angle of 0°. A value of 60° would be typical for an octahedron.<sup>[8,15]</sup> In addition, the  $\text{WS}_6$  core deviates less

from  $D_{3h}$  symmetry than the  $\text{WC}_6$  core found in the organometallic precursor.<sup>[6]</sup> The mean W–S bond length of 2.380 Å, interligand S...S distance of 3.111 Å and intraligand S...S distance of 3.123 Å are slightly longer than those reported for the isostructural  $\text{Mo}^{\text{VI}}$  complex [mean values:  $d(\text{Mo-S})$  2.367 Å,  $d(\text{S...S, interligand})$  3.091 Å,  $d(\text{S...S, intraligand})$  3.110 Å]. This observation can be explained by taking into account the slightly greater ionic radius of  $\text{W}^{\text{VI}}$  compared to that of  $\text{Mo}^{\text{VI}}$ . As expected, the average C–S bond length of 1.727 Å in **1** falls in the range observed for the isostructural molybdenum(vi) complex. As observed for the  $\text{Mo}^{\text{VI}}$  complex the  $\text{S}_2\text{C}_6\text{H}_4$  planes in **1** deviate from the  $\text{WS}_2$  planes (13.5°, 22.6°, 32.7°) thereby enforcing a deviation from ideal  $D_{3h}$  symmetry for the complex (Figure 2).

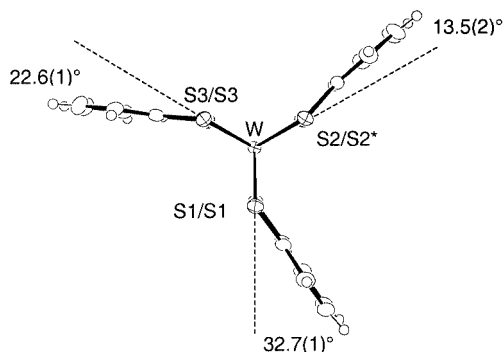


Figure 2. View of  $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  projected down the approximate molecular threefold axis, showing the bend of the ligands

A comparison of the molecular structures of the members of the series  $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{n-}$  ( $n = 0, 1, 2$ ) shows no clear correlation of electronic configuration or overall charge of the complexes and the molecular geometry. The one-electron reduction of trigonal-prismatic  $[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  results in pseudooctahedral  $[\text{W}^{\text{V}}(\text{S}_2\text{C}_6\text{H}_4)_3]$ ,<sup>[11]</sup> with an average twist angle of 33°. The pseudooctahedral coordination was also observed for the analogous  $\text{Mo}^{\text{V}}$  complex.<sup>[10]</sup> Here it was explained by the occupation of the  $\pi$ -antibonding  $4a_1'$  molecular orbital causing destabilization of both S...S interactions and M–S bonds and leading to an octahedral distortion.<sup>[10]</sup> Following this argument for the tungsten complexes, dianionic  $[\text{W}^{\text{IV}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{2-}$  should adopt a symmetry even closer to octahedral than the  $\text{W}^{\text{V}}$  complex due to the fully occupied  $4a_1'$  orbital. Surprisingly, this assumption was disproved by the close trigonal-prismatic structure found for  $[\text{W}^{\text{IV}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{2-}$ ,<sup>[12]</sup> with an average twist angle of only 3.5°. Table 1 summarizes structural parameters for the series  $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{n-}$  ( $n = 0, 1, 2$ ).

From the variation of the twist angles  $\Phi$  in the series  $[\text{M}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{n-}$  ( $\text{M} = \text{Mo}, \text{W}; n = 0, 1, 2$ ) it appears that the d-electron configuration is not the only governing principle for the formation of a certain coordination geometry. The  $\text{M}^{\text{VI}}$  complexes exhibit a trigonal-prismatic  $\text{WS}_6$  core and the one-electron reduction leads to a distorted octahedral geometry. Further reduction leads, at least in the case of  $\text{W}^{\text{IV}}$ , again to an almost trigonal-prismatic geometry. The recently reported structural characterization of two other tris(dithiolene) series<sup>[16]</sup>  $[\text{M}\{\text{S}_2\text{C}_2(\text{CH}_3)_2\}_3]^{n-}$

Table 1. Selected mean bond lengths and twist angles for the series  $[\text{W}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{n-}$  ( $n = 0, 1, 2$ )

	$[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{[a]}$	$[\text{W}^{\text{V}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{[b]}$	$[\text{W}^{\text{IV}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]^{2- [c]}$
W–S	2.380	2.386 (2.387)	2.391
S–S <sub>inter</sub>	3.111	3.227 (3.235)	3.139
S–S <sub>intra</sub>	3.123	3.101 (3.123)	3.101
C–S	1.744	1.713 (1.779)	1.750
Twist angle $\Phi$	0°	33°	3.5°

[a] This study. [b] Ref.;<sup>[11a]</sup> values in parentheses from ref.<sup>[11b]</sup> [c] Ref.<sup>[12]</sup>

( $M = \text{Mo}$ ,  $n = 0, -1, -2$ ;  $M = \text{W}$ ,  $n = -1, -2$ ) revealed distorted trigonal-prismatic structures for all members. These results indicate, once again, that the stabilization of the trigonal-prismatic structure is not only governed by electronic factors but must be considered a complicated process involving various factors.

## Experimental Section

**General Remarks:** Unless stated otherwise, all manipulations were carried out in an atmosphere of dry argon by means of standard Schlenk techniques. Diethyl ether and hexane were freshly distilled from Na-benzophenone prior to use.

**$[\text{W}^{\text{VI}}(\text{C}_6\text{H}_4\text{S}_2-1,2)_3]$  (1):**  $\text{WCl}_6$  (198 mg, 0.5 mmol) was suspended in dry diethyl ether (30 mL) and cooled to  $-78^\circ\text{C}$ . With vigorous stirring MeLi (2 mL of a 1.6 M solution in diethyl ether, 3.2 mmol) was added dropwise and the mixture was allowed to warm to  $-35^\circ\text{C}$ . After stirring for 3 h the red-brown reaction mixture was filtered through celite into a cold solution ( $-30^\circ\text{C}$ ) of benzene-1,2-dithiol (214 mg, 1.5 mmol) in diethyl ether (10 mL). The reaction mixture was allowed to warm to ambient temperature while methane gas evolved. The product was filtered, washed with diethyl ether (5 mL) and *n*-hexane (20 mL) and dried *in vacuo*. Yield 236 mg (77%).  $\text{C}_{18}\text{H}_{12}\text{S}_6\text{W}$  (604.50): calcd. C 35.76, H 2.00, S 31.82; found C 35.60, H 2.13, S 31.66. Additional spectroscopic parameters were identical to those reported in 1966.<sup>[2d]</sup> Crystals of **1** were obtained from a saturated dichloromethane solution.

**X-ray Crystallographic Study:** A suitable crystal ( $0.2 \times 0.2 \times 0.2 \text{ mm}^3$ ) was mounted on a Bruker AXS APEX diffractometer equipped with a Mo rotating anode ( $\lambda = 0.71073 \text{ \AA}$ ), a cooling device and graphite monochromator. 14512 Raw structure factors ( $-19 \leq h \leq 19$ ,  $-13 \leq k \leq 14$ ,  $-12 \leq l \leq 12$ ,  $2\theta = 4\text{--}45^\circ$ ) were collected at  $-120^\circ\text{C}$  using omega- and phi-scans. An empirical absorption correction was applied with SADABS<sup>[17]</sup> ( $T_{\text{min}}/T_{\text{max}} = 0.3379$ ) before merging. Complex **1** crystallized in the orthorhombic space group *Pnma*,  $a = 16.034(5)$ ,  $b = 11.793(4)$ ,  $c = 10.276(3) \text{ \AA}$ ,  $V = 1942.9(10) \text{ \AA}^3$ . Structure solution with SHELXS<sup>[18]</sup> and subsequent refinement of 139 parameters against 1516 observed [ $I > 2\sigma(I)$ , 1794 unique collected intensities] structure factors using SHELXL<sup>[19]</sup> with anisotropic thermal parameters for all non-hydrogen atoms revealed that the unit cell contains  $Z = 4$  molecules  $\text{C}_{18}\text{H}_{12}\text{S}_6\text{W}$  (604.49 g/mol,  $d_{\text{calcd.}} = 2.067 \text{ g/cm}^3$ ). The tungsten atom resides at a special position on a mirror plane. Hydrogen positions were determined by difference Fourier techniques and refined with isotropic thermal parameters. Final obtained residues  $R_{\text{all}} = 3.81$ ,  $R_{\text{obsd.}} = 2.94$ ,  $R_{\text{w,obsd.}} = 6.98\%$ , GOF = 1.036. ORTEP<sup>[20]</sup> was used for all drawings. CCDC-185593 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retriev](http://www.ccdc.cam.ac.uk/conts/retriev)

ing.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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