Supplementary Information.

Tungsten carbonyl σ-complexes with charge-compensated *nido*-carboranyl thioether ligands

Sergey V. Timofeev^{*}, Olga B. Zhidkova, Elena M. Mosolova, Igor B. Sivaev, Ivan A. Godovikov, Kyrill Yu. Suponitsky, Zoya A. Starikova, Vladimir I. Bregadze

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119991 Moscow, Russian Federation

Crystals of monoclinic form of 4 suitable for XRD study were obtained during crystallization from in $CDCl_3$ in NMR tube.

An asymmetric unit cell of the monoclinic form of complex 4 contains two independent molecules A and A' (Figure 1S). The main differences in the molecular structure of two independent molecules and that in orthorhombic modification is the orientation of SMe_2 substituent relative to carborane cage (Table 1S) that can be attributed to an influence of the crystal field. All the other geometry parameters are similar.

	Complex 4,	Complex 4,	Complex 4,
Torsion angle or Bond	Orthorhombic form	Monoclinic form,	Monoclinic form,
		molecule A	molecule A'
B9-B10-S3-C9	-168.8(3)	-70.1(4)	-157.2(4)
B9-B10-S3-C10	86.6(3)	-175.7(4)	97.5(5)
B11-C7-S1-C5	-48.0(3)	-38.0(4)	-52.9(4)
B9-C8-S2-C6	45.2(3)	39.5(4)	44.2(4)
W1-C1	1.966(4)	1.975(5)	1.963(5)
W1-C2	1.971(3)	1.974(5)	1.985(5)
W1-C3	2.034(3)	2.049(6)	2.020(5)
W1-C4	2.028(3)	2.004(5)	2.031(5)
W1-S1	2.5461(8)	2.5036(12)	2.5323(11)
W1-S2	2.5388(8)	2.5311(11)	2.5474(12)

Table 1S. Selected bonds and angles for two polymorh modifications of complex 4.



Figure 1S. The structures of two independent molecues (A - left, A' - right) of monoclinic modification of complex 4 with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

In Table 2S we have listed short and shortened intermolecular contacts for both polymorphs. It can be seen that only slightly shortened contacts are observed in the crystal structures of both polymorphs. Stabilization of their crystal structures is due to weak C-H...O, C-H...S and H...H contacts. From Table 2S one can see that weak C-H...O interactions are somewhat stronger in orthorhombic modification. At the same time, the C-H...S and H...H interactions contribute to a stabilization of monoclinic form. It is also seen that nearly all shortened contacts are observed between two independent molecules rather than for A...A and A'...A' molecular pairs which can be used as an expanation of the existance of two symmetrically independent molecules.

Shortened contact		MolMol	Symmetry code	Distance
Monoclinic modification				
04	H5'B	AA'	-1+x,y,z	2.597
04	H10'	AA'	-1+x,y,z	2.569
02	H9'B	AA'	x,y,z	2.520
H5B	O4'	AA'	x,y,1+z	2.604
01	H10G	AA'	-1.5+x,1/2-y,1/2+z	2.596
03	H10C	AA'	-1/2+x,1/2-y,1/2+z	2.614
S1	H5'C	AA'	x,y,z	2.943
S3	O2'	AA'	2-x,-y,1-z	3.234
O2'	S3	A'A	2-x,-y,1-z	3.234
O4'	H5B	A'A	x,y,-1+z	2.604
H5'B	O4	A'A	1+x,y,z	2.597
H10'	O4	A'A	1+x,y,z	2.569

Table 2S. Shortened intermolecular contacts (Å) for orthorhombic and monoclinic modifications of complex **4**.

H10C	03	A'A	1/2+x,1/2-y,-1/2+z	2.614
H10G	01	A'A	1.5+x,1/2-y,-1/2+z	2.596
H5'C	H6'A	A'A'	-1+x,y,z	2.255
H6'A	H5'C	A'A'	1+x,y,z	2.255
H2'	H10C	A'A'	-1/2+x,1/2-y,-1/2+z	2.285
H10C	H2'	A'A'	1/2+x,1/2-y,1/2+z	2.285
Orthorhombic modification				
H9A	O4		x,-1+y,-1+z	2.494
H10C	O4		x,-1+y,z	2.567
04	H10C		x,1+y,z	2.567
04	H9A		x,1+y,1+z	2.494
H9B	03		1/2-x,-1/2+y,-1/2+z	2.454
03	H9B		1/2-x,1/2+y,1/2+z	2.454

X-ray study of monoclinic form of complex 4 was carried out using SMART APEX2 CCD (λ (Mo-K_{α}) = 0.71073 Å, graphite monochromator, ω -scans) at 120K. Collected data were analized by the SAINT and SADABS programs incorporated into the APEX2 program package. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The positions of hydrogen atoms attached to the boron atoms were located in the difference Fourier maps and then normalized to 1.05Å. The H(C) positions were calculated. All the hydrogen atoms were refined in isotropic approximation by the riding model. The bridged H10 and H10' atoms were refined without any constraints. The refinement was carried out with the SHELXTL program. The details of data collection and crystal structures refinement are summarized in Table 3S. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 1048359.

Parameter	4 Monoclinic modification
Empirical formula	$C_{10}H_{21}B_9O_4S_3W$
Fw	582.59
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	7.3013(8)
b, Å	45.559(5)
<i>c</i> , Å	12.7794(14)
β , deg	91.404(2)
<i>V</i> , Å ³	4249.7(8)
Z	8

Table S3. Crystallographic data for monoclinic modification of compound

$d_{\rm calc},{\rm g}\cdot{\rm cm}^{-3}$	1.821	
μ, mm ⁻¹	5.774	
F(000)	2240	
θ range, deg.	1.79 - 27.00	
reflections collected	79818	
independent reflections	9209	
R _{int}	0.0516	
refined parameters	503	
Completeness to theta θ , %	99.2	
$GOF(F^2)$	1.214	
reflections with $I > 2\sigma(I)$	8502	
$R_1(F) (I \ge 2\sigma(I))^a$	0.0345	
$wR_2(F^2)$ (all data) ^b	0.0631	
Largest diff. peak/hole, e·Å-3	1.481 / -1.726	
^a $R_1 = \sum F_o - F_c / \sum (F_o);$ ^b $wR_2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2])^{1/2}$		