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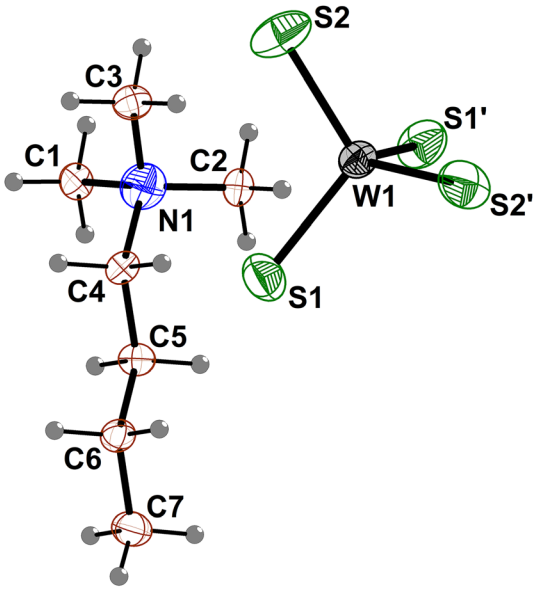
Crystal structure of bis(*N*,*N*,*N*-trimethylbutanaminium) tetrathiotungstate(VI), $(BuMe_3N)_2[WS_4]$



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Abstract

$C_{14}H_{36}N_2S_4W$, monoclinic, *C*2/*c* (no. 15), a = 16.175(3) Å, b = 9.7755(15) Å, c = 15.452(3) Å, β = 115.183(7)°, V = 2211.0(7) Å^3, Z = 4, $R_{gt}(F)$ = 0.0190, $wR_{ref}(F^2)$ = 0.0490, T = 223 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.32 × 0.22 × 0.21 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	5.60 mm^{-1}
Diffractometer, scan mode:	PHOTON III M14, φ and ω
θ_{max}, completeness:	28.3°, 98 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14,425, 2701, 0.046
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2659
$N(param)_{refined}$:	97
Programs:	Bruker,[1] SHELX,[2] WinGX/ORTEP,[3] Diamond[4]

1 Source of material

$(NH_4)_2WS_4$ (0.030 g, 0.086 mmol) and $BuMe_3NI$ (0.063 g, 0.26 mmol) were charged to a Pyrex tube with diameter of 9 mm and about 0.3 mL 1:2 (v/v) H_2O/MeOH mixture was added as a solvent. While the solvent was being frozen, the Pyrex tube was evacuated under vacuum and sealed with the use of a flame. The sealed tube was placed in an oven and heated at 90 °C for a day, then cooled to room temperature. Yellow orange polyhedral crystals were isolated by filtration and washed with MeOH and diethyl ether several times. Crystals of $(BuMe_3N)_2[WS_4]$ were obtained in 13 % yield, based on the W metal used.

2 Experimental details

H atoms were positioned geometrically and treated as riding, with C–H = 0.98 (CH_2) and 0.97 (CH_3) Å with U_{iso}(H) = 1.2 (1.5 for methyl) U_{eq}(C). H atoms of the CH_3 were positioned to be staggered with respect to the shortest other bond to the atom to which the CH_3 is attached.

3 Comment

The title compound, $(BuMe_3N)_2[WS_4]$, prepared by the solvothermal reaction of $(NH_4)_2WS_4$ and $BuMe_3NI$ with a 1:2 (v/v)

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
W1	1.0000	0.23270 (2)	0.7500	0.03188 (8)
S1	0.90589 (5)	0.10341 (8)	0.63454 (5)	0.05106 (17)
S2	1.07957 (5)	0.35925 (9)	0.69656 (6)	0.0591 (2)
N1	0.64017 (15)	0.3282 (2)	0.64921 (17)	0.0449 (5)
C1	0.6894 (3)	0.2240 (3)	0.6177 (3)	0.0586 (8)
H1A	0.6748	0.2376	0.5506	0.088*
H1B	0.6705	0.1330	0.6268	0.088*
H1C	0.7547	0.2337	0.6553	0.088*
C2	0.6635 (3)	0.3074 (5)	0.7525 (3)	0.0691 (9)
H2A	0.6441	0.2168	0.7618	0.104*
H2B	0.6326	0.3757	0.7736	0.104*
H2C	0.7290	0.3160	0.7894	0.104*
C3	0.6719 (3)	0.4673 (3)	0.6369 (3)	0.0658 (8)
H3A	0.6566	0.4828	0.5698	0.099*
H3B	0.7375	0.4736	0.6736	0.099*
H3C	0.6421	0.5358	0.6592	0.099*
C4	0.5377 (2)	0.3254 (3)	0.5861 (2)	0.0519 (6)
H4A	0.5094	0.4032	0.6030	0.062*
H4B	0.5277	0.3373	0.5193	0.062*
C5	0.4912 (2)	0.1972 (4)	0.5938 (3)	0.0585 (7)
H5A	0.5021	0.1828	0.6606	0.070*
H5B	0.5167	0.1190	0.5736	0.070*
C6	0.3894 (2)	0.2063 (4)	0.5317 (3)	0.0617 (8)
H6A	0.3640	0.2844	0.5522	0.074*
H6B	0.3787	0.2215	0.4651	0.074*
C7	0.3416 (3)	0.0772 (4)	0.5384 (3)	0.0773 (10)
H7A	0.2768	0.0847	0.4971	0.116*
H7B	0.3502	0.0639	0.6039	0.116*
H7C	0.3669	−0.0001	0.5185	0.116*

H_2O/MeOH mixture as the solvent, is composed of a $[WS_4]^{2-}$ molecular anion and two charge-balancing $BuMe_3N^+$ cations. Soluble tetrathiotungstate compounds have focused much attention mainly due to their potential as precursors for the WS_2 HDS (HydroDeSulfurization) catalyst and the soft synthesis of WS_2 nanomaterials.[5,6] The tetrathiotungstate $[WS_4]^{2-}$ anion had been stabilized and structurally characterized with a number of cations such as NH_4^+,[7,8] Rb^+,[9] $[Ni(tren)_2]^{2+}$ (*tren* = tris(2-aminoethyl)amine),[10] tetraalkylammonium (Me_4N^+, Et_4N^+, Pr_4N^+),[11] and Ph_4P^+,[12] as well as organic ammonium with N–H bonds present ($H_3NCH_2CH_2NH_3^{2+}$, *i*–Pr NH_3^+, etc.).[13–17] As an unsymmetrical mixed tetraalkylammonium cation, $BuMe_3N^+$ can be considered a new type of cation suitable for the stabilization of the $[WS_4]^{2-}$ anion. It is noteworthy that attempts to obtain $(PhMe_3N)_2[WS_4]$ using the same solvothermal synthetic approach resulted in the stabilization of the $[W_3OS_8]^{2-}$ anion instead of the $[WS_4]^{2-}$ anion.[18]

In the $(BuMe_3N)_2[WS_4]$ compound, the structure of the discrete $[WS_4]^{2-}$ anion shows that the central W(1) atom lies on a twofold axis and only two S atoms, S(1) and S(2) are crystallographically unique. The tetrahedral coordination behavior around the W(1) atom is quite ideal as S–W–S bond angles range from 108.54(3) to 111.02(5)° and W–S distances are nearly identical ranging from 2.1846(7) to 2.1877(7) Å. The ideal tetrahedral coordination behavior of the $[WS_4]^{2-}$ anion implies that there is minimal influence caused by the packing of unsymmetrical $BuMe_3N^+$ cations and no strong interaction between the $BuMe_3N^+$ cations and the $[WS_4]^{2-}$ anions. Compared to the shortest S···H distance of 2.31 Å observed in $((CH_3)H_2NCH_2CH_2NH_3)[WS_4]$,[17] the shortest S···H distance in this compound is significantly longer, measuring 2.8477(9) Å between S(1) and H(2B), indicating a lack of H-bonding between the $BuMe_3N^+$ cations and the $[WS_4]^{2-}$ anions.

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Competing interests: The authors declare no conflicts of interest regarding this article.

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References

1. Bruker. *APEX3 and SAINT–Plus*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2016.
2. Sheldrick, G. M. Crystal Structure Refinement with *SHELXL*. *Acta Crystallogr.* **2015**, *C71*, 3–8.
3. Farrugia, L. J. *WinGX* and *ORTEP* for Windows: An Update. *J. Appl. Crystallogr.* **2012**, *45*, 849–854.
4. Brandenburg, K. *DIAMOND. Visual Crystal Structure Information System*; Crystal Impact: Bonn, Germany, 2015.
5. Chianelli, R. R. Fundamental Studies of Transition Metal Sulfide Hydrodesulfurization Catalysts. *Catal. Rev. Sci. Eng.* **1984**, *26*, 361–393.
6. Li, Y. D.; Li, X. L.; He, R. R.; Zhu, J.; Deng, Z. X. Artificial Lamellar Mesostructures to WS_2 Nanotubes. *J. Am. Chem. Soc.* **2002**, *124*, 1411–1416.
7. Sasvári, K. The Crystal Structure of Ammonium thiotungstate $(NH_4)_2WS_4$. *Acta Crystallogr.* **1963**, *16*, 719–724.
8. Srinivasan, B. R.; Poisot, M.; Näther, C.; Bensch, W. Diammonium tetrathiotungstate(VI), $(NH_4)_2[WS_4]$, at 150 K. *Acta Crystallogr.* **2004**, *E60*, i136–i138.
9. Yao, J.; Ibers J. A. Dirubidium tetrathiotungstate, $Rb_2[WS_4]$. *Acta Crystallogr.* **2004**, *E60*, i10–i11.
10. Ellermeier, J.; Stähler, R.; Bensch, W. Two New $[Ni(tren)_2]^{2+}$ Complexes: $[Ni(tren)_2]Cl_2$ and $[Ni(tren)_2]WS_4$. *Acta Crystallogr.* **2002**, *C58*, m70–m73.
11. Poisot, M.; Näther, C.; Bensch, W. Synthesis, Spectroscopic and X-Ray Structure Characterisation of Bis(tetramethylammonium), Bis(Tetraethylammonium) and Bis(tetrapropylammonium) tetrathiotungstates. *Z. Naturforsch.* **2006**, *61b*, 1061–1066.
12. Bailen, P. L.; Powell, A. V.; Vaqueiro, P. Bis(Tetraphenylphosphonium) tetrasulfidotungstate(VI). *Acta Crystallogr.* **2008**, *E64*, m574.

13. Srinivasan, B. R.; Dhuri, S. N.; Näther, C.; Bensch, W. Ethylenediammonium tetrathiotungstate(VI). *Acta Crystallogr.* **2002**, *E58*, m622–m624.
14. Srinivasan, B. R.; Dhuri, S. N.; Näther, C.; Bensch, W. 1,3-Propanediammonium tetrathiotungstate and *N*,*N*,*N*′,*N*′-Tetramethylethylenediammonium tetrathiotungstate. *Acta Crystallogr.* **2003**, *C59*, m124–m127.
15. Srinivasan, B. R.; Dhuri, S. N.; Näther, C.; Bensch, W. 1,4-Dimethylpiperazinium tetrathiotungstate(VI). *Acta Crystallogr.* **2003**, *E59*, m681–m683.
16. Srinivasan, B. R.; Dhuri, S. N.; Näther, C.; Bensch, W. Synthesis, X-Ray Structures, Spectroscopic and Thermal Characterization of Two New Organic Ammonium tetrathiotungstates. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1087–1094.
17. Srinivasan, B. R.; Näther, C.; Dhuri, S. N.; Bensch, W. On the Importance of H-Bonding Interactions in Organic Ammonium Tetrathiotungstates. *Monatsh. Chem.* **2006**, *137*, 397–411.
18. Kim, K.-W.; Kim, S. Crystal Structure of Bis(trimethylphenylammonium) aquaoxidooctathiotritungstate, $(Me_3PhN)_2[W_3OS_8(H_2O)]$. *Z. Kristallogr. N. Cryst. Struct.* **2023**, *238*, 389–390.