

1,4-Dimethylpiperazinium tetrathiotungstate(VI)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(C-C)$ = 0.004 Å
R factor = 0.025
wR factor = 0.067
Data-to-parameter ratio = 24.8

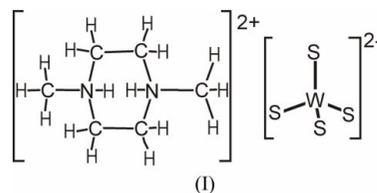
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex, $(C_6H_{16}N_2)[WS_4]$, consists of tetrahedral $[WS_4]^{2-}$ dianions and organic dications. There are two crystallographically independent 1,4-dimethylpiperazinium ($1,4-dmpH_2$) dications in the asymmetric unit, both of which are located around a centre of inversion, while the anions are located in general positions. The anions and cations are connected by hydrogen bonding.

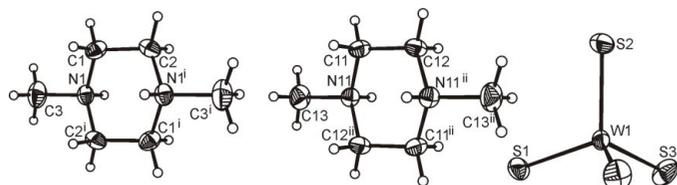
Received 7 July 2003
Accepted 21 July 2003
Online 31 July 2003

Comment

The sulfur complexes of the group 6 metals Mo (Cocouvanis, 1998) and W (Shibahara, 1993) are a unique class of compounds, encompassing an unusually wide range of metal:sulfur stoichiometries, metal oxidation states, coordination geometries and different bonding modes of the sulfide ligands. The tetrahedral $[MS_4]^{2-}$ ($M = Mo$ or W) complexes are routinely used as the starting material for the preparation of a variety of structurally diverse di-, tri- and tetranuclear $M-S$ complexes. In addition, it has been reported that piperidinium tetrathiotungstate (Dhar & Chandrasekaran, 1989) and benzyltriethylammonium tetrathiomolybdate (Prabhu *et al.*, 2000) can be used as sulfur-transfer reagents in organic synthesis, for the formation of novel organosulfur complexes under mild conditions.



The present contribution is part of our ongoing investigations aimed at the synthesis and structural characterization of new thiomolybdates and thiotungstates. Representative examples of complexes structurally characterized by us in earlier work, containing the tetrahedral $[MS_4]^{2-}$ moiety, include $[Ni(en)_3][MS_4]$ (*en* is 1,2-diaminoethane) (Ellermeier *et al.*, 1999; Ellermeier, 2002) $[Co_2(tren)_3][MoS_4]_2$ [*tren* is tris(2-aminoethyl)amine] (Ellermeier & Bensch, 2001), $[Mn(dien)_2][MoS_4]$ (*dien* is diethylenetriamine) (Ellermeier & Bensch, 2002), $[Ni(tren)_2][WS_4]$ (Ellermeier *et al.*, 2002), $(C_2H_{10}N_2)[MoS_4]$ (Srinivasan *et al.*, 2001), $(C_2H_{10}N_2)[WS_4]$ (Srinivasan *et al.*, 2002) $(C_3H_{12}N_2)[WS_4]$ and $(C_6H_{18}N_2)[WS_4]$ (Srinivasan *et al.*, 2003). The facile formation of such complexes in aqueous amine media not only indicates the stability of the $[MS_4]^{2-}$ core in basic solution but also is a testimony to the flexibility of the $[MS_4]$ tetrahedron to adapt


Figure 1

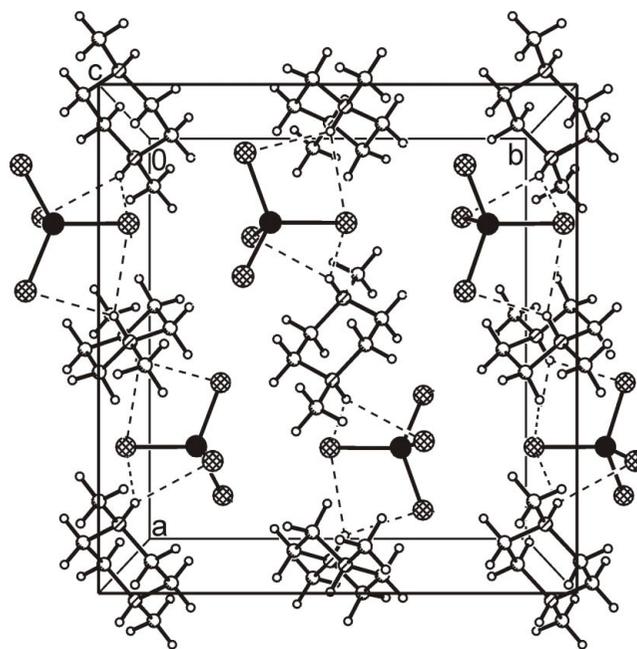
The crystal structure of 1,4-dimethylpiperazinium tetrathiotungstate, with labelling and with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$].

to different structural environments. In almost all these complexes, the $[MS_4]$ tetrahedron is slightly distorted, with one or two of the $M-S$ bonds elongated, which we have explained on the basis of the strength and numbers of hydrogen-bonding interactions between the $[MS_4]^{2-}$ dianion and the organic cation. The hydrogen-bonding interactions can be tuned by choosing cations (amines) which contain different numbers of potential hydrogen-bonding donors.

In order to understand the effect of crystal packing forces and the factors responsible for the elongation of the $M-S$ bond lengths, it is desirable to perform a statistical evaluation of the structural parameters of several such complexes containing this structural motif. The results of such an analysis may yield information for the usage of the $[MS_4]$ moiety in the powerful field of crystal engineering (Desiraju, 1989). For progress in this field we are in search of new $[MS_4]^{2-}$ complexes in different structural environments. The title complex is a new addition to the growing list of structurally characterized tetrathiotungstates. The cyclic diamine 1,4-dimethylpiperazine (1,4-dmp) used in this work has the same number of potential hydrogen bonding donors as in the acyclic diamine N,N,N',N' -tetramethylethylenediamine (tmen) employed in our earlier report (Srinivasan *et al.*, 2003).

The structure of (I) contains discrete $[1,4\text{-dmpH}_2]^{2+}$ cations and $[WS_4]^{2-}$ anions (Fig. 1). There are two crystallographically independent 1,4-dimethylpiperazinium dications in the asymmetric unit, both of which are located around a centre of inversion, while the anions are located in general positions. The bond lengths and bond angles of the $[1,4\text{-dmpH}_2]^{2+}$ cation in (I) are in good agreement with those reported for other compounds containing this cation (Farrell *et al.*, 2001). The $[WS_4]$ tetrahedron in (I) is moderately distorted, with $S-W-S$ angles between $108.32(3)$ and $111.67(4)^\circ$. The $W-S$ bond lengths range from $2.1781(8)$ to $2.2136(8)$ Å (Table 1), with a mean $W-S$ distance of 2.1943 Å. All structural parameters of (I) are in good agreement with those reported for other compounds containing the $[WS_4]^{2-}$ moiety, such as $[\text{Ni}(\text{tren})_2][WS_4]$ (Ellermeier *et al.*, 2002), $(\text{enH}_2)[WS_4]$ (Srinivasan *et al.*, 2002), and $(1,3\text{-pnH}_2)[WS_4]$ and $(\text{tmenH}_2)[WS_4]$ (Srinivasan *et al.*, 2003).

The cations and anions are further connected *via* hydrogen bonding between the S atoms and the H atoms bound to nitrogen (Fig. 2). As a result, layers are formed which are parallel to (010). Detailed analysis of the hydrogen-bonding pattern indicates that the differing $W-S$ bond distances in (I) can be attributed to the different numbers and strengths of $N-H \cdots S$ interactions. In all, four short intermolecular $S \cdots H$


Figure 2

The crystal structure of 1,4-dimethylpiperazinium tetrathiotungstate, viewed along the c axis (intermolecular hydrogen bonding is shown as dashed lines).

contacts are observed in (I), with $N \cdots S$ distances ranging from $3.347(3)$ to $3.489(2)$ Å (Table 2). Atoms S1 and S2 each make one contact, while S4 has two short contacts. The shortest $W-S$ distance of $2.1781(8)$ Å is observed for S3, which is not involved in any hydrogen bonding. Although atom S4 has two short contacts with an average $N \cdots S$ distance of 3.4785 Å, they are relatively long compared to the shortest distance, 3.347 Å, between S2 and N1. This observation suggests that a short hydrogen bond influences the $W-S$ distances more strongly than two medium long $H \cdots S$ contacts and therefore may explain why $W-S_2$ is longer than $W-S_4$. To our knowledge, the $W-S$ distance of $2.2136(8)$ Å observed in (I) is one of the longest $W-S$ bonds known in tetrathiotungstates and is comparable with the $W-S$ bond length of $2.212(9)$ Å reported for $[\text{Ni}(\text{tren})_2][WS_4]$ (Ellermeier *et al.*, 2002).

The present structural examination of (I), together with our results reported previously, indicate that hydrogen-bonding interactions between the anions and cations are one of the factors determining the $M-S$ bond lengths. However, a detailed statistical analysis of the structural data of more such complexes, which differ in terms of the number of hydrogen-bonding contacts, is desirable to fully comprehend this phenomenon. Efforts in this direction are underway.

Experimental

$(\text{NH}_4)_2[WS_4]$ (348 mg, 1 mmol) was dissolved in distilled water (10 ml) and the solution filtered. To the clear yellow filtrate, the organic diamine 1,4-dmp (0.6 ml) was added and the reaction mixture left aside for crystallization. After 2 d, well formed yellow blocks of (I) were obtained. The crystals were filtered, washed with ice-cold water (5 ml) followed by 2-propanol (10 ml) and ether (20 ml), and air-dried [yield 70% (based on W)]. The crystals are stable in air.

Crystal data

 $(\text{C}_6\text{H}_{16}\text{N}_2)[\text{WS}_4]$ $M_r = 428.30$ Orthorhombic, *Pbca* $a = 13.3792$ (11) Å $b = 12.6369$ (7) Å $c = 14.9381$ (9) Å $V = 2525.6$ (3) Å³ $Z = 8$ $D_x = 2.253$ Mg m⁻³

Data collection

Stoe IPDS diffractometer

 φ scansAbsorption correction: numerical
(*X-SHAPE* and *X-RED*; Stoe &
Cie, 1998) $T_{\min} = 0.360$, $T_{\max} = 0.555$

23034 measured reflections

Mo $K\alpha$ radiationCell parameters from 8000
reflections $\theta = 15$ – 23° $\mu = 9.77$ mm⁻¹ $T = 293$ (2) K

Block, yellow

 $0.14 \times 0.09 \times 0.06$ mm

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.025$ $wR(F^2) = 0.067$ $S = 1.01$

2946 reflections

119 parameters

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0453P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.004$ $\Delta\rho_{\max} = 1.66$ e Å⁻³ $\Delta\rho_{\min} = -1.39$ e Å⁻³Extinction correction: *SHELXL97*

Extinction coefficient: 0.00187 (9)

Table 1

Selected geometric parameters (Å, °).

W1–S3	2.1781 (8)	C1–C2	1.514 (5)
W1–S1	2.1866 (7)	C2–N1 ⁱ	1.495 (4)
W1–S4	2.1988 (12)	N11–C13	1.499 (4)
W1–S2	2.2136 (8)	N11–C12 ⁱⁱ	1.500 (4)
N1–C3	1.491 (4)	N11–C11	1.502 (4)
N1–C2 ⁱ	1.495 (4)	C11–C12	1.512 (5)
N1–C1	1.497 (4)	C12–N11 ⁱⁱ	1.500 (4)
S3–W1–S1	111.67 (4)	C2 ⁱ –N1–C1	110.4 (2)
S3–W1–S4	108.48 (3)	N1–C1–C2	111.5 (2)
S1–W1–S4	108.46 (3)	N1 ⁱ –C2–C1	110.3 (3)
S3–W1–S2	110.88 (4)	C13–N11–C12 ⁱⁱ	111.1 (2)
S1–W1–S2	108.94 (3)	C13–N11–C11	111.1 (3)
S4–W1–S2	108.32 (3)	C12 ⁱⁱ –N11–C11	110.4 (2)
C3–N1–C2 ⁱ	111.4 (3)	N11–C11–C12	110.7 (3)
C3–N1–C1	110.8 (3)	N11 ⁱⁱ –C12–C11	111.3 (2)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1–H1 ⁱⁱⁱ –S2	0.91	2.64	3.347 (3)	135
N1–H1 ⁱⁱⁱ –S4	0.91	2.73	3.489 (2)	141
N11–H11 ⁱⁱⁱ –S1 ⁱⁱⁱ	0.91	2.69	3.427 (3)	139
N11–H11 ⁱⁱⁱ –S4 ⁱⁱⁱ	0.91	2.73	3.468 (2)	139

Symmetry code: (iii) $\frac{1}{2} + x, y, \frac{1}{2} - z$.

The C–H and N–H H atoms were positioned with idealized geometry [N–H = 0.91 Å, C–H(methylene) = 0.97 Å and C–H(methyl) = 0.96 Å] and refined with fixed isotropic displacement parameters using a riding model [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{methylene}}/\text{N–H})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$]. The largest peak in the residual electron density map of 1.66 e Å⁻³ is located 0.06 Å from W1 and the deepest hole of -1.39 e Å⁻³ is located 0.82 Å from W1

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP in SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB in SHELXL97*.

This work is supported by the state of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft. BRS thanks the University Grants Commission, New Delhi, for funds and the Deutscher Akademischer Austauschdienst (DAAD), Bonn, for a visiting fellowship.

References

- Bruker (1998) *SHELXTL*. Version 5.10. Bruker AXS Inc. Madison, Wisconsin, USA.
- Coucovanis, D. (1998). *Adv. Inorg. Chem.* **45**, 1–73.
- Desiraju, G. R. (1989). *Crystal Engineering: The Design of Organic Solids*. Materials Science Monographs 54. Amsterdam: Elsevier.
- Dhar, P. & Chandrasekaran, S. (1989). *J. Org. Chem.* **54**, 2998–3000.
- Ellermeier, J. (2002). PhD Dissertation, University of Kiel, Germany.
- Ellermeier, J. & Bensch, W. (2001). *Z. Naturforsch. Teil B*, **56**, 611–619.
- Ellermeier, J. & Bensch, W. (2002). *Monatsh. Chem.* **133**, 945–957.
- Ellermeier, J., Näther, C. & Bensch, W. (1999). *Acta Cryst.* **C55**, 501–503.
- Ellermeier, J., Stähler, R. & Bensch, W. (2002). *Acta Cryst.* **C58**, m70–m73.
- Farrell, D. M. M., Ferguson G., Lough, A. L. & Glidewell, C. (2001). *Acta Cryst.* **C57**, 952–954.
- Prabhu, K. R., Shivanand, P. S. & Chandrasekaran, S. (2000). *Angew. Chem. Int. Ed. Engl.* **39**, 4316–4318.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Shibahara, T. (1993). *Coord. Chem. Rev.* **123**, 73–147.
- Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2002). *Acta Cryst.* **E58**, m622–m624.
- Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2003). *Acta Cryst.* **C59**, m124–m127.
- Srinivasan, B. R., Vernekar, B. K. & Nagarajan, K. (2001). *Indian J. Chem. Sect. A*, **40**, 563–567.
- Stoe & Cie (1998). *X-SHAPE* (Version 1.03), *X-RED* (Version 1.03) and *IPDS* (Version 2.89). Stoe & Cie, Darmstadt, Germany.