Ethylenediammonium tetrathiotungstate(VI)

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The structure of the title complex, $(C_2H_{10}N_2)[WS_4]$, consists of tetrahedral $[WS_4]^{2-}$ anions which are connected to the organic ethylenediammonium dications *via* hydrogen bonding. All atoms are located in general positions.

Comment

Since the first reported synthesis of an $[Ni(WS_4)_2]^{2-}$ complex (Müller & Diemann, 1971), an extensive chemistry of the sulfide complexes of W, and also the lighter congener Mo, has been developed. The $[WS_4]^{2-}$ ion has been used as a reagent for the synthesis of several structurally diverse W–S complexes, such as $[W_2(S)_2(\mu\text{-}S)_2(S_4)_2]^{2-}$ (Cohen & Stiefel, 1985), $[W_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$ (Manoli *et al.*, 1987), $[W_2(S)_2$-$(SH)(\mu\text{-}\eta^3\text{-}S_2)(\eta^2\text{-}S_2)_3]^-$ (Sécheresse *et al.*, 1986), $[W(WS_4)_2]^{2-}$ (Bhaduri & Ibers, 1986), $[SW(WS_4)_2]^{2-}$, $[W_3S_{10}]^{2-}$ (Müller *et al.*, 1989) and $[(W_2S_4)(WS_4)_2]^{2-}$ (Sécheresse *et al.*, 1982). A compound with composition $[W_4S_8(en)_4]S$ (en is ethylenediamine) was obtained by the reaction of K_2S_4 with $W(CO)_6$ in supercritical ethylenediamine; it contains as the main structural feature a W_4 tetrahedron with each face bridged by a μ_3-S atom (Woods *et al.*, 1993). The synthesis and structural characterization of such complexes clearly demonstrates the versatile coordination behavior of the sulfide ligand towards W in various oxidation states. In addition, it has been shown that the $[WS_4]^{2-}$ ion can act as a bidentate ligand, leading to the formation of sulfur-bridged heterometallic complexes (Müller *et al.*, 1981). The interest in this area is due to the fact that sulfide complexes of W, such as $[Ni(tren)_2]WS_4$ [tren is tris(2-aminoethylamine); Ellermeier *et al.*, 2002], and also of Mo, such as $[Ni(en)_3]MoS_4$ (Ellermeier *et al.*, 1999), can be synthesized as phase-pure products in good yields under mild solvothermal conditions.

$$[H_3N\text{-}CH_2\text{-}CH_2\text{-}NH_3]^{2+} \ [WS_4]^{2-}$$
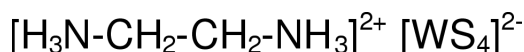
$$(I)$$

The study of the $[WS_4]^{2-}$ and $[MoS_4]^{2-}$ salts of organic cations has gained importance in recent years in view of the reported observations that piperidinium tetrathiotungstate (Dhar & Chandrasekaran, 1989) and benzyltriethyl-ammonium tetrathiomolybdate can be used as sulfur-transfer reagents in organic synthesis, for the formation of novel organosulfur compounds under mild reaction conditions (Prabhu *et al.*, 2000). The study of the reactivity characteristics of sulfide complexes of Mo and W with organic bases, such as en, can also be useful for understanding the influence of the chemical properties of the solvent on product formation under
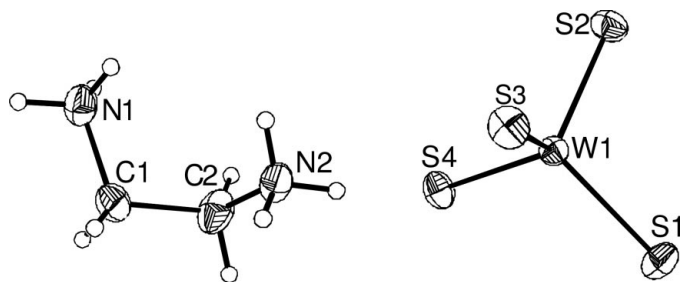
Figure 1
The crystal structure of ethylenediammonium tetrathiotungstate(VI), with labeling and with 50% probability displacement ellipsoids.

Figure 2
The crystal structure of ethylenediammonium tetrathiotungstate(VI), viewed along the c axis. Hydrogen bonds are shown as dotted lines.

solvothermal conditions. Recently, we reported the synthesis and structural characterization of $(enH_2)[MoS_4]$ (en is 1,2-ethylenediamine), as part of a project on the synthesis and reactivity characterization of the salts of thiomolybdates and thiotungstates of organic dications (Srinivasan *et al.*, 2001). In continuation of this work, we have undertaken the structure determination of the title compound, (I).

The title compound is isostructural with the earlier reported Mo analog. The lattice parameters show a very small increase of the a, b and c values compared to those of the corresponding Mo analog. The substitution of Mo by W results in only a slight increase in the unit-cell volume [the unit-cell volume of the Mo complex is 938.7 (9) $Å^3$]. This can be explained on the basis of the larger size of W. The structure consists of $(enH_2)^{2+}$ cations and tetrahedral $[WS_4]^{2-}$ anions (Fig. 1). The cations and anions are further connected *via* weak hydrogen bonds (Fig. 2). The WS_4 tetrahedron is very slightly distorted, with S—W—S angles ranging from 108.66 (7) to 110.08 (6)°. The W—S bond distances vary from 2.1851 (14) to 2.1943 (13) Å. In contrast, the W—S distances in the complex $[Ni(tren)_2][WS_4]$ range from 2.1580 (10) to 2.2122 (9) Å, while the S—W—S angles vary from 108.39 (4) to 110.78 (4)° (Ellermeier *et al.*, 2002). These differences can be attributed to the differing nature of the cations. The W—S bond lengths are slightly longer than the average W—S bond length of 2.177 Å in $(NH_4)_2[WS_4]$ (Müller *et al.*, 1981). The significantly longer W—S distance of 2.2122 (9) Å in the complex $[Ni(tren)_2][WS_4]$ has earlier been attributed to hydrogen-bonding interactions of the S atom with the H atoms of the tren ligands. This postulate gains further credence from the present results. In the title compound, atom S3 is 2.1943 (13) Å from the central W and is involved in three short contacts to the H atoms of the $(enH_2)^{2+}$ cation. In all, nine short intermolecular contacts between the S atoms of $[WS_4]^{2-}$ and the H atoms of the $(enH_2)^{2+}$ cation, ranging from 2.432 to 3.003 Å, are observed. Six of these intermolecular contacts are shorter than the shortest intermolecular contact of 2.73 (4) Å observed in the complex $[Ni(tren)_2][WS_4]$. The reason for this is that the N atom in (I) carries a positive charge, while the N atom in the tren ligand of $[Ni(tren)_2][WS_4]$ is neutral and coordinated to Ni^{II}. Short intermolecular contacts have also been observed between the amino H atoms of the coordinated en ligand and the S atoms of $[Ni(en)_3][MoS_4]$, ranging from
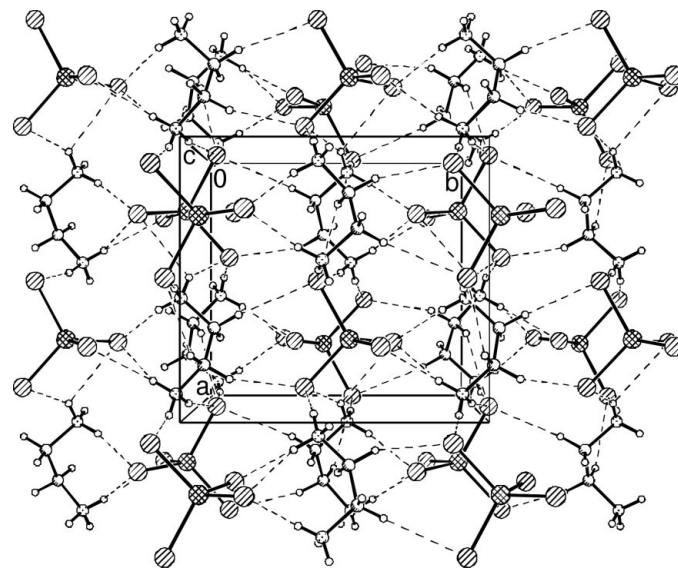
2.653 (3) to 2.680 (3) Å (Ellermeier *et al.*, 1999). In (I), at least five intermolecular contacts are observed which are shorter than 2.653 (3) Å.

The title compound has been synthesized by reacting $(NH_4)_2[WS_4]$ with en. In contrast, the acidification reactions of $[WS_4]^{2-}$ have been shown to result in the formation of di-, tri- and tetranuclear W–S complexes, such as $[W_2S_{11}H]^-$, $[W_2S_{11}]^{2-}$, $[W_3S_8]^{2-}$, $[W_3S_9]^{2-}$, $[W_3S_{10}]^{2-}$, $[W_4S_{12}]^{2-}$ *etc.*, as mentioned earlier. Thus, the present work indicates that the tetrahedral $[WS_4]^{2-}$ core is stable under alkaline conditions and remains intact. The use of the strong base en results in a simple cation exchange. Further studies are in progress to understand such base-promoted cation exchange reactions by employing different organic bases.

Experimental

$(NH_4)_2[WS_4]$ (1 mmol) was dissolved in 6 ml distilled water and 0.2 ml 99% ethylenediamine was added at room temperature. The reaction mixture was filtered and the clear filtrate was allowed to stand undisturbed in a 50 ml glass beaker in a refrigerator. After 2 d, crystals of (I) crystallized out. The orange–yellow crystals were filtered off, washed with 5 ml cold water and dried in air. Yield: 60%. The crystals are stable in air.

Crystal data

$(C_2H_{10}N_2)[WS_4]$	Mo $K\alpha$ radiation
$M_r = 374.21$	Cell parameters from 8000
Orthorhombic, $P2_12_12_1$	reflections
$a = 8.6401$ (4) Å	$\theta = 8$–25°
$b = 9.3228$ (5) Å	$\mu = 12.93$ mm^{-1}
$c = 11.8281$ (7) Å	$T = 293$ (2) K
$V = 952.75$ (9) Å^3	Plate, yellow
$Z = 4$	$0.13 \times 0.10 \times 0.05$ mm
$D_x = 2.609$ Mg m^{-3}	

Data collection

Stoe IPDS diffractometer	2207 reflections with $I > 2\sigma(I)$
φ scans	$R_{int} = 0.040$
Absorption correction: numerical	$\theta_{max} = 28.1°$
(*X-SHAPE*; Stoe & Cie, 1998)	$h = -11 \rightarrow 11$
$T_{min} = 0.237$, $T_{max} = 0.527$	$k = -12 \rightarrow 12$
8270 measured reflections	$l = -15 \rightarrow 15$
2308 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$\Delta\rho_{max} = 1.44$ e Å^{-3}
$wR(F^2) = 0.054$	$\Delta\rho_{min} = -2.17$ e Å^{-3}
$S = 1.04$	Extinction correction: *SHELXL*97
2308 reflections	Extinction coefficient: 0.0101 (4)
83 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	960 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$	Flack parameter = −0.011 (11)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

W1—S4	2.1851 (14)	N1—C1	1.483 (8)
W1—S2	2.1852 (13)	C1—C2	1.500 (9)
W1—S1	2.1927 (14)	C2—N2	1.468 (8)
W1—S3	2.1943 (13)		
S4—W1—S2	109.23 (6)	S2—W1—S3	109.60 (6)
S4—W1—S1	108.66 (7)	S1—W1—S3	110.08 (6)
S2—W1—S1	109.46 (6)	N1—C1—C2	112.8 (5)
S4—W1—S3	109.78 (6)	N2—C2—C1	113.3 (5)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N1$\cdots$S4^{i}	0.89	2.48	3.274 (5)	149
N1—H1N1$\cdots$S2^{i}	0.89	3.00	3.478 (6)	115
N1—H2N1$\cdots$S1^{ii}	0.89	2.44	3.300 (6)	161
N1—H3N1$\cdots$S2^{iii}	0.89	2.69	3.370 (6)	134
N1—H3N1$\cdots$S3^{iii}	0.89	2.80	3.558 (6)	144
N2—H1N3$\cdots$S4	0.89	2.47	3.254 (5)	147
N2—H1N3$\cdots$S3	0.89	2.85	3.424 (6)	124
N2—H2N3$\cdots$S1^{iv}	0.89	2.43	3.301 (5)	166
N2—H3N3$\cdots$S3^{iii}	0.89	2.55	3.385 (6)	157

Symmetry codes: (i) $\frac{3}{2} - x, 2 - y, \frac{1}{2} + z$; (ii) $1 + x, y, z$; (iii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (iv) $\frac{1}{2} - x, 2 - y, \frac{1}{2} + z$.

The H atoms were located from a difference map, but were positioned with idealized geometry ($d_{C-H} = 0.97$ Å and $d_{N-H} = 0.89$ Å) and refined with constrained isotropic displacement parameters [$U_{iso}(H) = 1.5U_{eq}(C,N)$], using a riding model.

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXL*97.

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