4484 measured reflections
4217 independent reflections

3 standard reflections
every 300 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.133$
$S = 1.000$
4217 reflections
429 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 2P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.506$ e Å^{-3}
$\Delta\rho_{min} = -0.921$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

V1—O1	1.6073 (19)	O4—C1	1.426 (3)
V1—O2	1.6215 (18)	O5—C2	1.215 (3)
V1—O4$^{\text{i}}$	1.9596 (17)	C1—C3	1.518 (3)
V1—O3	1.9749 (18)	C1—C4	1.519 (4)
V1—O4	1.9983 (17)	C1—C2	1.522 (3)
O3—C2	1.297 (3)		
O1—V1—O2	108.57 (10)	O2—V1—O4	136.21 (9)
O1—V1—O4$^{\text{i}}$	103.96 (9)	O4'—V1—O4	70.62 (8)
O2—V1—O4$^{\text{i}}$	99.32 (9)	O3—V1—O4	76.58 (7)
O1—V1—O3	100.99 (9)	C2—O3—V1	120.24 (16)
O2—V1—O3	95.65 (9)	C1—O4—V1$^{\text{i}}$	132.01 (14)
O4'—V1—O3	144.90 (7)	C1—O4—V1	117.84 (14)
O1—V1—O4	115.22 (9)	V1'—O4—V1	109.38 (8)

Symmetry code: (i) $1 - x, 1 - y, -z$.

The phase problem was solved by direct methods using *SHELX97* (Sheldrick, 1997), which was also used to refine the structure.

Data collection: Kuma KM-4 software. Cell refinement: Kuma KM-4 software. Data reduction: Kuma KM-4 software. Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELX97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1343). Services for accessing these data are described at the back of the journal.

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Tetraethylammonium (1-Pyrrolidinecarbodithioato-S,S')(tetrathiotungstenio-S,S')-nickelate(1−)

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Abstract

In the title nickel–tungsten sulfido mixed-metal complex {tetraethylammonium (1-pyrrolidinecarbodithioato-$2\kappa^2S,S'$)-di-μ-thio-$1:2\kappa^4S$-dithio-$1\kappa^2S$-nickeltungsten(Ni—W), [N(C$_2$H$_5$)$_4$][NiWS$_4$(S$_2$CNC$_4$H$_8$)]}, the Ni atom is fourfold coordinated by a pyrrolidine-derived dithiocarbamate and a tetrathiotungstate moiety. Dithiocarbamate and tetrathiotungstate act as bidentate ligands, each chelating *via* two S atoms to the Ni atom, thus producing an approximately square-planar geometry. The Ni—W distance is 2.761 (1) Å and the Ni—S$_{bridge}$—W angles are 77.13 (8) and 77.08 (9)°. The four Ni—S distances are identical within s.u.'s and average 2.205 (3) Å. The WS$_4$ moiety is a distorted tetrahedron, with S—W—S angles ranging from 102.3 (1) to 111.8 (1)°. The two terminal W—S distances are 2.149 (3) and 2.151 (3) Å, while the bridging W—S distances are 2.221 (2) and 2.226 (3) Å.

Comment

Recently, interesting non-linear optical (NLO) properties have been discovered for Group 6–Group 11 sulfido clusters (Hou *et al.*, 1996). To find compounds of Group 6 with superior NLO properties, we have synthesized a series of Group 6–Group 10 sulfido compounds (Long *et al.*, 1996, 1997). We report here the structure of a nickel–tungsten sulfido mixed-metal complex, (I).

(I)
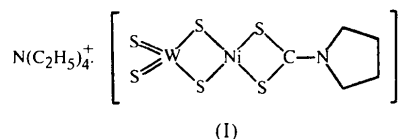
The structure of (I) consists of isolated cations and bimetallic anions (Fig. 1). The Ni atom is four-coordinate: a dithiocarbamate and a tetrathiotungstate each acts as a bidentate ligand, coordinating *via* two S atoms. The geometry of the 1-pyrrolidinecarbodithioate ligand is similar to that found in the complex [Ni(S$_2$CN-

$C_4H_8)_2$] (Engelhardt *et al.*, 1985), but with a slightly smaller S—C—S angle {108.4 (5)° in (I) and 110.7 (2)° in [Ni($S_2CNC_4H_8)_2$]}; the S—C distances are typical.
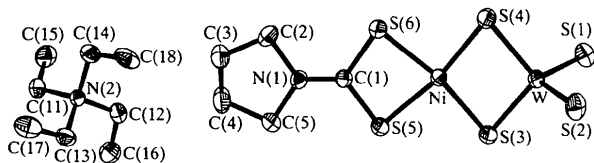

Fig. 1. A view of the title molecule. Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity.

The Ni and the four coordinated S atoms are approximately coplanar, with no deviations larger than 0.15 Å. The S(5)—Ni—S(6) angle is restricted to 78.3 (1)° by the bite angle of the dithioate; it is much smaller than the other three *cis*-S—Ni—S angles, but is close to the angle of 79.33 (5)° found in [Ni($S_2CNC_4H_8)_2$] (Engelhardt *et al.*, 1985). Owing to the nickel–tungsten interaction, the S(3)—Ni—S(4) angle is opened to 103.3 (1)°, becoming the largest of the four *cis*-S—Ni—S angles. The four Ni—S bond distances [2.202 (3)–2.209 (3) Å] are almost identical and comparable to the mean Ni—S distance of 2.206 (1) Å in [Ni($S_2CNC_4H_8)_2$], but smaller than those of 2.237 (4) Å in [Ni($WS_4)_2$]$^{2-}$ (Mueller *et al.*, 1981) and 2.295 (8) Å in [(C_4Me_4)Ni(PMe_2Ph){(μ-S)$_2WS_2$}] (Howard *et al.*, 1990).

The WS_4 moiety is a distorted tetrahedron, similar to that of [Ni($WS_4)_2$]$^{2-}$ (Mueller *et al.*, 1981). Except for the S_{bridge}—W—S_{bridge} bond angle of 102.3 (1)°, the other five S—W—S angles are normal for a tetrahedron, ranging from 109.0 (1) to 111.8 (1)°. The W—$S_{terminal}$ distances are near to those of 2.150 (5) and 2.151 (4) Å found in [Ni($WS_4)_2$]$^{2-}$ and slightly shorter than those found in ($NH_4)_2$[WS_4] (mean 2.165 Å) (Sasvari, 1983). The two W—S_{bridge} bonds are significantly longer than the W—$S_{terminal}$ bonds, as in related compounds (Mueller *et al.*, 1981; Howard *et al.*, 1990). A considerable difference between the W—S_{bridge} bond distances in the title compound and those in ($NH_4)_2$[WS_4] is a consequence of the coordination of WS_4 to nickel.

Experimental

The title compound was produced by ligand replacement between [Ni($S_2CNC_4H_8)_2$] and ($NH_4)_2$[WS_4] in the presence of Et_4NCl in dichloromethane solution. Brown–green crystals were obtained from the resultant solution after diffusion of 2-propanol.

Crystal data

$(C_8H_{20}N)[NiWS_4(C_5H_8NS_2)]$
$M_r = 647.3$
Monoclinic
$P2_1/c$
$a = 13.610 (4)$ Å
$b = 8.286 (1)$ Å
$c = 19.848 (4)$ Å
$\beta = 93.74 (2)°$
$V = 2233.5 (8)$ Å^3
$Z = 4$
$D_x = 1.92$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11–13°$
$\mu = 6.55$ mm^{-1}
$T = 293$ K
Lath
$0.32 \times 0.18 \times 0.06$ mm
Brown–green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scan (North *et al.*, 1968)
$T_{min} = 0.271$, $T_{max} = 0.675$
4395 measured reflections
4230 independent reflections

3170 reflections with $I > 3\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 9$
$l = -23 \rightarrow 23$
3 standard reflections frequency: 60 min intensity variation: 0.6%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.047$
$S = 0.69$
3170 reflections
208 parameters
H atoms: see below
$w = 1/[\sigma^2(F) + (0.020F)^2 + 1.0] - F$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.00$ e Å^{-3}
(1.05 Å from W)
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

W—Ni	2.761 (1)	Ni—S(4)	2.206 (3)
W—S(1)	2.149 (3)	Ni—S(5)	2.204 (3)
W—S(2)	2.151 (3)	Ni—S(6)	2.202 (3)
W—S(3)	2.221 (2)	S(5)—C(1)	1.717 (9)
W—S(4)	2.226 (3)	S(6)—C(1)	1.711 (9)
Ni—S(3)	2.209 (3)		
S(1)—W—S(2)	109.0 (1)	S(4)—Ni—S(6)	89.6 (1)
S(1)—W—S(3)	111.1 (1)	S(5)—Ni—S(6)	78.3 (1)
S(1)—W—S(4)	111.2 (1)	W—S(3)—Ni	77.13 (8)
S(2)—W—S(3)	111.3 (1)	W—S(4)—Ni	77.08 (9)
S(2)—W—S(4)	111.8 (1)	Ni—S(5)—C(1)	86.6 (3)
S(3)—W—S(4)	102.3 (1)	Ni—S(6)—C(1)	86.7 (3)
S(3)—Ni—S(4)	103.3 (1)	S(5)—C(1)—S(6)	108.4 (5)
S(3)—Ni—S(5)	89.4 (1)	S(5)—C(1)—N(1)	125.1 (7)
S(3)—Ni—S(6)	166.3 (1)	S(6)—C(1)—N(1)	126.4 (7)
S(4)—Ni—S(5)	166.0 (1)		

The structure was solved by direct methods and expanded using Fourier techniques. H atoms were placed at calculated positions (C—H = 0.95 Å) and refined in riding mode.

Data collection, cell refinement and data reduction: *CAD*-4 *Software* (Enraf–Nonius, 1989). Program(s) used to solve and refine structure: *MolEN* (Fair, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN* and *GCIF* (Chen, 1996).

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1,4-Butanediammonium Tetrabromopalladate(II)

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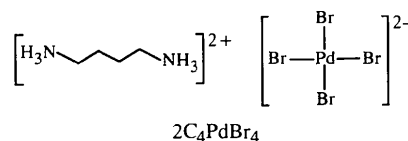
Abstract

The title structure, $(C_4H_{14}N_2)[PdBr_4]$, presents a two-dimensional arrangement of alternating mineral layers composed of $[PdBr_4]^{2-}$ units and organic layers containing 1,4-butanediammonium chains $[NH_3\text{-}(CH_2)_4\text{-}NH_3]^{2+}$. The $[PdBr_4]^{2-}$ units are square planar and are disposed nearly perpendicular to the crystallographic *bc* plane. The organic chains are centrosymmetric and are characterized by a left-handed conformation at both

ends. The link between the organic and mineral moieties is achieved by N—H⋯Br hydrogen bonds. No phase transition before the decomposition temperature has been detected by powder X-ray diffraction *versus* temperature and differential scanning calorimetry.

Comment

Extensive studies have been carried out on the crystal structures, phase transitions and physical properties of two-dimensional perovskite-like compounds of the families $(RNH_3)_2MX_4$ and $[NH_3\text{-}R'\text{-}NH_3]MX_4$, and related materials (M = Cd, Mn, Pb, Cu; X = Cl, Br; R and R' are organic radicals). The few palladium compounds of these families which have been structurally characterized are some chloride derivatives: $(C_3H_7NH_3)_2[PdCl_4]$ (Willett & Willett, 1977), $[NH_3\text{-}(CH_2)_2\text{-}NH_3][PdCl_4]$ (Berg & Søtofte, 1976) and $[NH_3\text{-}(CH_2)_4\text{-}NH_3][PdCl_4]$ (Maris *et al.*, 1996). As part of our study of phase transitions in the 1,4-butanediammonium tetrahalogenometalate(II) series (Khechoubi *et al.*, 1994; Courseille *et al.*, 1994), we report here the crystal structure at room temperature of the palladium–bromine compound $[NH_3\text{-}(CH_2)_4\text{-}NH_3][PdBr_4]$ (hereafter 2C$_4$PdBr$_4$).

$$\left[H_3N\diagdown\diagup\diagdown NH_3\right]^{2+} \quad \left[\begin{array}{c} Br \\ | \\ Br-Pd-Br \\ | \\ Br \end{array}\right]^{2-}$$

2C$_4$PdBr$_4$

The crystallographic organization can be described as a succession of organic and inorganic layers. The inorganic layer consists of discrete $[PdBr_4]^{2-}$ anions which pack to form a puckered two-dimensional network. The Pd atom lies on an inversion center and displays a square-planar coordination of the four Br atoms. The Pd—Br distances [2.4422 (9) and 2.4529 (9) Å] are comparable with the distance observed in the tetragonal compound K$_2$PdBr$_4$ [2.444 (3) Å; Martin *et al.*, 1975].

A short Pd⋯Br contact of 3.2712 (10) Å was detected (Table 2). Similar contacts are found for $[CuCl_4]^{2-}$, $[CuBr_4]^{2-}$ (Garland *et al.*, 1990) and $[PdCl_4]^{2-}$ salts (Maris *et al.*, 1996). For copper derivatives, these contacts result from an octahedral distortion explained by a Jahn–Teller effect in relation to the electronic configuration of the Cu^{2+} ions. The Pd^{2+} ions are generally known to adopt square-planar coordination geometry. Willett & Willett (1977) have also observed such a contact in $(C_3H_7NH_3)_2[PdCl_4]$ and have interpreted this interaction as a weak repulsive one. However, in 2C$_4$PdBr$_4$, this weak interaction contributes to the formation of a two-dimensional network in the inorganic layer resulting in a packing close to a perovskite-like structure.

The cations also lie on inversion centers and adopt a left-handed conformation at both ends (*gtg'* confor-