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TETRAKIS(Ν,N-DIETHYL-DITHIOCARBAMATO)TUNGSTEN(V)BROMIDE, C_{20}H_{40}BrΝ_{4}S_{8}W

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Preliminary information. In recent years, the interest in dithiocarbamato compounds of molybdenum and tungsten has grown and various tetrakis(dithiocarbamato)molybdenum(IV) compounds have been published (Jowitt and Mitchell, 1968; Smith and Brown, 1970; Bradley and Chisholm, 1971; Brown and Smith, 1972). Oxidation of tetrakis(dithiocarbamato)molybdenum(IV) has been reported to result in the formation of compounds containing tetrakis(dithiocarbamato)molybdenum(V) anions (Rowbottom and Wilkinson, 1973; Nieuwpoort, Moonen and Cras, 1973), which also could be prepared via a direct way (Nieuwpoort, 1973). This method can be used to prepare the corresponding tungsten(V) compound (Nieuwpoort, 1974). To clarify some properties of the compounds and gain some insight on the coordination polyhedron, the crystal structure analysis of tetrakis(Ν,N-diethyl-dithiocarbamato)tungsten(V)bromide (abbreviated as W(dtc)_{4}Br) was undertaken.

Crystal data. From single crystal diffractometer data (CuKα, λ=1.5418Å):

a=10.693(4), b=28.02(1), c=11.170(5)Å, β=92.92(3)°, V=3342.4Å³.

Space group P 2₁/c from systematic absences. D_{m}=1.72g/cm³, D_{c}=1.70g/cm³ for Z=4. P.W.=856.84.

Intensity data, structure determination and refinement.
The intensities were measured with Ni-filtered Cu-radiation on a Nonius automatic diffractometer (θ-2θ scan). Of the 2033 independent reflections...
theoretically attainable within the limit $\theta = 40^\circ$, 1589 reflections having $I > 3\sigma(I)$ ($\sigma(I)$ being calculated from counting statistics) were used in the analysis. Lorentz and polarisation corrections were performed in the usual way. Absorption corrections were not calculated ($\mu(CuK\alpha)=127.2\text{cm}^{-1}$).

The structure was solved by means of three-dimensional Patterson and Fourier syntheses and refined by full-matrix least-squares methods. The function that was minimized was $\sum (|F_o|-|F_c|)^2$ with $w=(\sigma^2(F_o)+(0.05|F_o|)^2)^{-1}$, where $\sigma^2(F_o)$ being calculated from counting statistics. Anisotropic thermal parameters were introduced for the heavy atoms W and Br. The atomic scattering factors used were those of W, Br, S, N, C and H as given in the International Tables for X-ray Crystallography(1962). Parameter shifts in the last refinement cycle were only a small fraction of the standard deviations. Final conventional R-value: 0.065.
Atomic coordinates (with e.s.d.)

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
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<td>C(14)</td>
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<td>0.0951(3)</td>
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<td>0.325(1)</td>
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<td>0.287(2)</td>
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<td>0.3322(3)</td>
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<td>0.077(3)</td>
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<td>C(12)</td>
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</tbody>
</table>
Bond distances and angles (with e.s.d.)

\[ W-S(A1) = 2.524(7) \text{ Å} \]
\[ W-S(B1) = 2.490(7) \text{ Å} \]
\[ W-S(A2) = 2.517(6) \text{ Å} \]
\[ W-S(B2) = 2.507(7) \text{ Å} \]
\[ S(A1)-W-S(B1) = 67.7(2)^\circ \]
\[ W-S(A1)-C(11) = 91.3(9)^\circ \]
\[ W-S(B1)-C(11) = 90.7(9)^\circ \]
\[ S(A2)-W-S(B2) = 67.4(2)^\circ \]
\[ W-S(A2)-C(21) = 90.1(8)^\circ \]
\[ W-S(B2)-C(21) = 89.0(8)^\circ \]

\[ 1 = 1.66(3) \text{ Å} \]
\[ 2 = 1.74(3) \text{ Å} \]
\[ 3 = 1.34(3) \text{ Å} \]
\[ 4 = 1.71(4) \text{ Å} \]
\[ 5 = 1.53(5) \text{ Å} \]
\[ 6 = 1.51(4) \text{ Å} \]
\[ 7 = 1.52(4) \text{ Å} \]

1,2 = 110(1)^\circ
1,3 = 126(2)^\circ
2,3 = 124(2)^\circ
3,4 = 119(2)^\circ
3,6 = 122(2)^\circ
4,6 = 118(2)^\circ
4,5 = 92(2)^\circ
6,7 = 111(2)^\circ

Comments. The tungsten atom is bonded to eight sulphur atoms from four chelating (dtc) ligands. The coordination geometry approximates very closely to triangularly dodecahedral. Similar coordination has been found in the \( \text{Ti(dtc)}_4 \) molecule (Colapietro et al., 1972) while different eight-coordination geometry has been found in \( \text{Th(dtc)}_4 \) and \( \text{NET}_4 \text{Np(dtc)}_4 \) (Brown et al., 1970).
The ideal model of dodecahedral coordination geometry ($D_{2d}$, $I2m$ symmetry) is described by Hoard and Silverton(1963). Chelation in the present compound is along the m edges (Hoard and Silverton notation). The dihedral angle between the trapezoidal least-squares best planes, which form the dodecahedron, is 89.3°. The following distances are averages (with the r.m.s. deviations from the mean): bond distances $W$-$S(A)$ 2.524(7), $W$-$S(B)$ 2.494(11); dodecahedron edges $S(A)$-$S(B)$ (intraligand) 2.80(1), $S(A)$-$S(B)$ (interligand) 3.22(3), $S(A)$-$S(A)$ 2.87(11), $S(B)$-$S(B)$ 3.61(4) Å. Corresponding to the very short interligand non-bonding S-S contacts in the Ti($dtc$)$_4$ molecule and in Mo(NO)($S^2CNBu^+$)$_3$ (Brennan and Bernal, 1970) the interligand $S(A)$-$S(B)$ and $S(A)$-$S(A)$ contact in the present compound are much shorter than the normal van der Waals distance.

The bromine atom is situated between five different ligands with shortest distances:

$$\begin{align*}
\text{Br-C(22)} &= 3.78(3) \text{ Å} \\
\text{Br-C(1h)} &= 3.63(3) \\n\text{Br-C(34)} &= 3.62(3) \\n\text{Br-C(32)} &= 3.53(3) \\n\text{Br-C(32)} &= 3.60(3)
\end{align*}$$

i 1-x, 1-y, 1-z

ii -x, 1-y, -z

iii 1-x, 1-y, -z

iv -x, $\frac{1}{2}$+y, $\frac{1}{2}$-z

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References.


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