

Pyridine–pyridine π – π stacking interactions in pentacarbonyl[pyridine-4(1*H*)-thione]tungsten(0)

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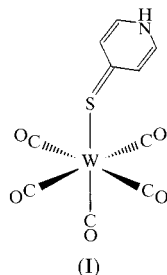
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In the title compound, $[\text{W}(\text{C}_5\text{H}_5\text{NS})(\text{CO})_5]$, the pyridine-4-thiol ligand coordinates through the sulfur in the thione mode. The coordination sphere around the W atom is distorted from octahedral geometry by intermolecular hydrogen bonding and steric interactions between the pyridine ring and two CO ligands. An intermolecular pyridine–pyridine ring distance of 3.47 (1) Å indicates π – π stacking interactions between these ligand units.

Comment

Pyridine-4-thiol has been widely used as a ligand in transition metal complexes where it can act as a monodentate ligand to one metal or a bridging ligand to two metals (Bajaj *et al.*, 1998; Coe *et al.*, 1998; Maekawa *et al.*, 1998; Paw *et al.*, 1998). It exists mainly as the pyridine-4(1*H*)-thione tautomer in solution (Etter *et al.*, 1992). Recently, pyridine-4-thiol attracted considerable attention because of its relevance as an electron promoter in the redox chemistry of cytochrome c (Hinnen & Niki, 1989) and also because of its self-assembly as monolayers on gold electrodes (Zhong *et al.*, 1999). Although X-ray structural studies of pyridine-4-thione in the $[\text{RuCl}(\text{pdma})_2(\text{pyridine-4-thione})]\text{PF}_6$ [pdma = *o*-phenylenebis(dimethylarsine)] (Coe *et al.*, 1997) and $[\text{Pd}_2(\mu\text{-dppm})_2(\text{pyridine-4-thione})](\text{ClO}_4)_2$, (dppm = diphenylphosphinomethane)



(Maekawa *et al.*, 1998) complexes have been reported previously, neither compound exhibits hydrogen bonding or

π – π pyridine interactions as occurs in $(\text{CO})_5\text{W}(\text{pyridine-4-thione})$, (I), as described herein.

The molecular structure of (I) (Fig. 1) shows that the S atom of a pyridine-4(1*H*)-thione ligand is coordinated to the tungsten. The W–S bond length of 2.557 (2) Å is similar to the W–S distances observed in the $\text{W}(\text{CO})_5(2\text{-thiouracilate})$ anion [2.533 (3) Å; Darensbourg *et al.*, 1999] and in $\text{W}(\text{CO})_5(\text{pyridine-2-thione})$ [2.568 (2) Å; Broomhead *et al.*, 1986]. The geometry about tungsten is distorted octahedral, with an S–W–C11 angle of 171.5 (1)°. This distortion appears to be due to steric repulsion between the pyridine ring and two CO ligands, as well as hydrogen bonding between the pyridinium N–H and the O11 atom of an adjacent molecule. Fig. 2 depicts a ball-and-stick representation of the hydrogen-bonding motif. It is interesting that the hydrogen bonding exhibited by $\text{W}(\text{CO})_5(\text{pyridine-2-thione})$ is of a different type (N–H...S bonds forming a cyclic dimer) than that seen in $\text{W}(\text{CO})_5(\text{pyridine-4-thione})$; however, the two crystals do have the same space group and similar cell constants.

The intermolecular hydrogen-bonding distance of N–H...O11(–1 + x , $\frac{3}{2} - y$, $-\frac{1}{2} + z$) is 2.15 Å, the N–H...O11 angle is 158°, and the N...O1 distance is 2.983 (5) Å. This hydrogen bonding increases the C11–W–C13 angle [92.8 (2)°] and decreases the C11–W–C14 angle [86.7 (1)°]. In the pyridine-4-thione ligand, the C–S bond distance [1.719 (4) Å] suggests considerable double-bond character. Mean C–S bond lengths in thiol and thione crystal structures from the Cambridge Structural Database are 1.81 (2) and 1.66 (4) Å, respectively (Etter *et al.*, 1992). It is also noteworthy that the C4–S distance [1.719 (4) Å] is longer than that of free pyridine-4(1*H*)-thione [1.703 (2) Å], which indicates a decrease in C–S π -bonding upon complexation.

The pyridine ring, which approximately bisects two CO ligands, is nearly planar, with an average standard deviation from planarity of the ring atoms of 0.01 Å. The S atom is in the pyridine ring plane. The C4–S–W angle is 117.9 (2)°, which suggests sp^2 hybridization of the S atom. The angle between the W–S vector and the pyridine ring plane is 8 (1)°. The C2–N–C6 angle of 121.5 (4)° is larger than that of the corresponding bond angles in di-2-pyridyl disulfide which range from 116 to 119° (Raghavan & Seff, 1977). This widening of the C2–N–C6 angle is attributed to the presence of the proton on the N atom. The corresponding angle in pyridine hydrochloride is 128° (Rérat, 1962). Singh (1965) proposed the empirical rule that the angle at a protonated N atom in a six-membered ring will be 125 (3)°, while the angle at an unprotonated nitrogen will be 116 (3)°. The C3–C4 [1.397 (6) Å] and C4–C5 [1.417 (6) Å] carbon–carbon lengths of the ring are slightly longer than those of C2–C3 [1.378 (6) Å] and C5–C6 [1.351 (6) Å]; this difference in C–C bond lengths is not as pronounced as in free pyridine-4(1*H*)-thione (Etter *et al.*, 1992): 1.419 (3), 1.419 (3) versus 1.375 (3), 1.368 (3) Å. The C–N bond lengths [1.334 (6) and 1.352 (6) Å, respectively] are similar to those [1.346 (3) Å] in free pyridine-4(1*H*)-thione (Etter *et al.*, 1992). These distances in (I) are consistent with some localized single and double bonding, but there is considerable delocalization in the pyri-

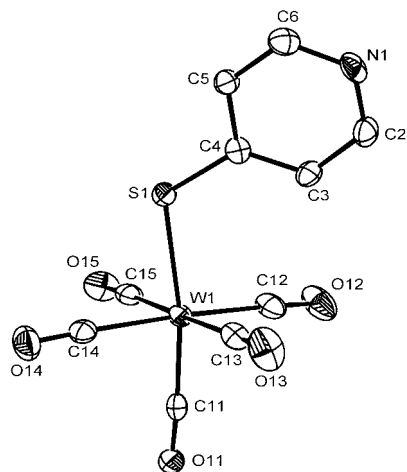


Figure 1
The structure of (I) showing 50% probability displacement ellipsoids and the atomic numbering scheme.

dine ring, more than is found in free pyridine-4(1*H*)-thione. The overall structure of the pyridine-4(1*H*)-thione moiety in (I) is similar to that found in the free ligand and in its other complexes (Coe *et al.*, 1997; Maekawa *et al.*, 1998).

In the $W(CO)_5$ moiety, the $W-C11$ bond [1.945 (5) Å] is shorter than the $W-CO$ bonds to the four equatorial CO groups, which have an average $W-C$ bond length of 2.044 (5) Å. The short $W-C11$ bond is due to increased π -back bonding from the W atom to the CO ligand *trans* to the S atom.

An examination of the packing diagram in Fig. 2 shows an intermolecular pyridine–pyridine ring distance of 3.47 (1) Å, indicative of π - π stacking interactions. The π - π stacking interactions are stronger than those of $W(CO)_5$ (pyridine-2-thione), in which the intermolecular pyridine–pyridine ring distance is 3.64 (1) Å (Broomhead *et al.*, 1986). Also important to the crystal packing are the $N-H \cdots O$ hydrogen bonds,

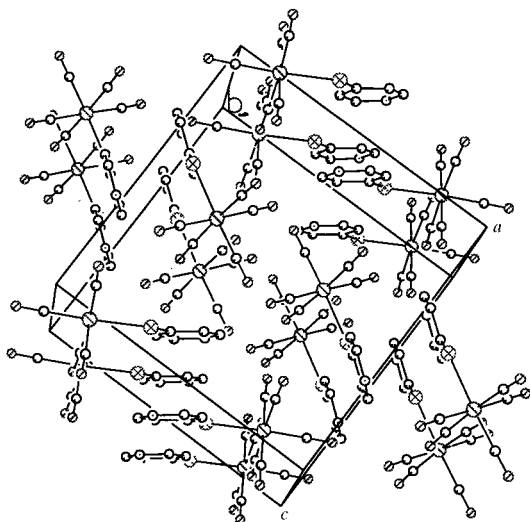


Figure 2
The molecular packing diagram of (I).

which give rise to hydrogen-bonded chains of *c*-glide-related molecules. The chains are related to one another by inversion centers. Thus, $N-H \cdots O$ hydrogen bonding and pyridine–pyridine π - π interactions dominate the crystal packing in the structure.

Experimental

The title compound was synthesized by substitution of the weakly coordinated tetrahydrofuran (thf) ligand with pyridine-4-thiol. A yellow solution of $W(CO)_5(thf)$ was prepared (Choi & Angelici, 1991) by photolysis (450 W Ace-Hanovia lamp) of $W(CO)_6$ (500 mg, 1.42 mmol) in tetrahydrofuran (40 ml). Addition of pyridine-4-thiol (150 mg, 1.35 mmol) to the $W(CO)_5(thf)$ solution causes the color to change from yellow to orange. The resulting orange solution was stirred for 2 h at room temperature and then evaporated under vacuum. The residue was dissolved in CH_2Cl_2 and chromatographed on a neutral alumina column (1 × 15 cm). The yellow–orange fraction was collected and concentrated under vacuum to give orange microcrystals of (I) (382 mg, 65% yield). Crystals were obtained by layering hexanes onto a solution of (I) in CH_2Cl_2 at 253 K. Analysis calculated for $C_{10}H_5O_5NSW$: C 27.61, H 1.16, N 3.13%; found: C 27.86, H 1.18, N 3.17%. 1H NMR ($CDCl_3$): 7.47 (*br t*, 2,6H), 7.71 (*d*, 3,5H), 9.4 (*br s*, NH) p.p.m.

Crystal data

$[W(C_5H_5NS)(CO)_5]$
 $M_r = 435.06$
Monoclinic, $P2_1/c$
 $a = 7.227$ (1) Å
 $b = 13.256$ (1) Å
 $c = 13.191$ (1) Å
 $\beta = 99.189$ (1)°
 $V = 1247.4$ (2) Å³
 $Z = 4$

$D_x = 2.317$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2167 reflections
 $\theta = 2-26^\circ$
 $\mu = 9.44$ mm⁻¹
 $T = 173$ (2) K
Block, orange
0.28 × 0.16 × 0.16 mm

Data collection

Siemens SMART CCD diffractometer
 φ and ω scans
Absorption correction: empirical (*SADABS*; Siemens, 1995)
 $T_{min} = 0.12$, $T_{max} = 0.22$
9890 measured reflections
2537 independent reflections

2167 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.038$
 $\theta_{max} = 26.37^\circ$
 $h = -9 \rightarrow 9$
 $k = -16 \rightarrow 16$
 $l = -16 \rightarrow 16$
Intensity decay: <1%

Table 1
Selected geometric parameters (Å, °).

W1–S1	2.5566 (12)	C13–O13	1.121 (6)
W1–C11	1.945 (5)	C14–O14	1.140 (5)
W1–C12	2.033 (5)	C15–O15	1.154 (6)
W1–C13	2.063 (5)	C2–C3	1.378 (6)
W1–C14	2.048 (5)	C3–C4	1.397 (6)
W1–C15	2.033 (5)	C4–C5	1.417 (6)
S1–C4	1.719 (4)	C5–C6	1.351 (6)
C11–O11	1.176 (5)	N1–C2	1.334 (6)
C12–O12	1.146 (6)	N1–C6	1.352 (6)
S1–W1–C11	171.40 (12)	C11–W1–C12	89.44 (18)
S1–W1–C12	98.29 (14)	C11–W1–C13	92.84 (18)
S1–W1–C13	90.86 (14)	C11–W1–C14	86.69 (17)
S1–W1–C14	85.45 (13)	C11–W1–C15	88.60 (18)
S1–W1–C15	87.66 (13)	C2–N1–C6	121.5 (4)
C4–S1–W1	117.91 (16)		

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.054$
 $S = 1.03$
2537 reflections
163 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0283P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.36 \text{ e } \text{\AA}^{-3}$

Except for some residual density in the region of the W1 atom (deepest hole at 0.79 Å from W), the final difference map showed no significant features.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1522). Services for accessing these data are described at the back of the journal.

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