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# Bis[(3,5-dimethylpyrazol-1-yl)ethyl] disulfide

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**Key indicators**

Single-crystal X-ray study
*T* = 150 K
Mean σ(C–C) = 0.003 Å
*R* factor = 0.038
*wR* factor = 0.101
Data-to-parameter ratio = 19.9

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



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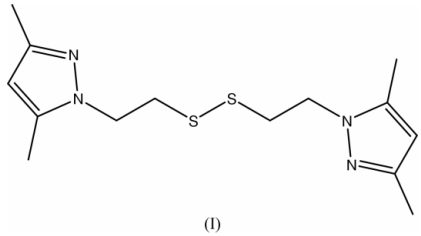
In the title compound, $C_{14}H_{22}N_4S_2$, a diethyl disulfide bridge containing an S—S bond of 2.0396 (6) Å connects two 3,5-dimethylpyrazole rings *via* the N1 atoms. The disulfide molecules are linked by weak C—H···π(pyrazole) interactions into chains that propagate along the *b* direction.

## Comment

Well-defined transition metal complexes with heteroatom-donor ligands can serve as viable models for the active sites of metalloenzymes (Darensbourg *et al.*, 2000; Kaasjager *et al.*, 1998; Sellmann *et al.*, 2002). Our goal is to synthesize a dinuclear Ni—Fe complex that resembles the S-bridged Ni—Fe unit of the [NiFe]-hydrogenases (Darensbourg *et al.*, 2000). The N,S-chelating ligand 1-(2-sulfanylethyl)-3,5-dimethylpyrazole (Hetdmp), which contains a thiol group to mimic cysteine residues, is well suited for this application (Bouwman & Reedijk, 1998). Colourless needles of the title compound, bis[(3,5-dimethylpyrazol-1-yl)ethyl] disulfide [or 1,1′-dithiodiethylenebis(3,5-dimethylpyrazole)], (I), the product of ligand oxidation, were isolated in our attempts to crystallize [Ni(etdmp)$_2$], a mononuclear precursor to the desired Ni—Fe model compound.



(I)

A view of (I) is presented in Fig. 1, and selected geometric parameters are listed in Table 1. In (I), two 3,5-dimethylpyrazole rings are connected, *via* N11 and N21 (N1 of the two rings by IUPAC convention), by a diethyl disulfide bridge. The bond lengths and angles involving the disulfide group [S—S = 2.0396 (6) Å, S—C = 1.8097 (15)/1.8156 (16) Å, C—S—S = 103.95 (6)/105.73 (6)° and C—S—S—C = 81.87 (8)°] are consistent with those observed in other disulfides, for example, bis(2,4-imidazolidinedione-5-ethyl) disulfide [Mullica *et al.*, 1998; S—S = 2.022 (4) Å, S—C = 1.801 (7)/1.817 (7) Å, C—S—S = 103.1 (3)/103.9 (3)° and C—S—S—C = −79.6 (3)°]. The diethyl disulfide bridge in (I) adopts a spiral conformation [S—S—C—C = 54.12 (12)/68.12 (12)°], and the attached pyrazole N atoms are oriented *gauche* [N11—C16—C17—S1 = 65.69 (16)°] and *anti* [N21—C26—C27—S2 = −176.75 (10)°] with respect to the disulfide bond. Thus, the pyrazole rings are nearly parallel, the dihedral angle between their planes being 6.26 (10)°. Although the two 1-thioethylene-3,5-dimethyl-

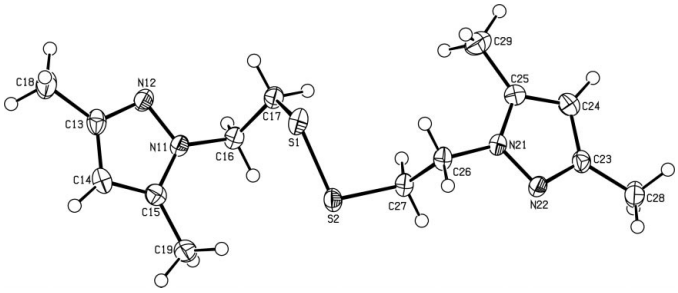



**Figure 1**
*PLATON*/*ORTEP* representation (Spek, 2003) of (I), with displacement ellipsoids at the 50% probability level.

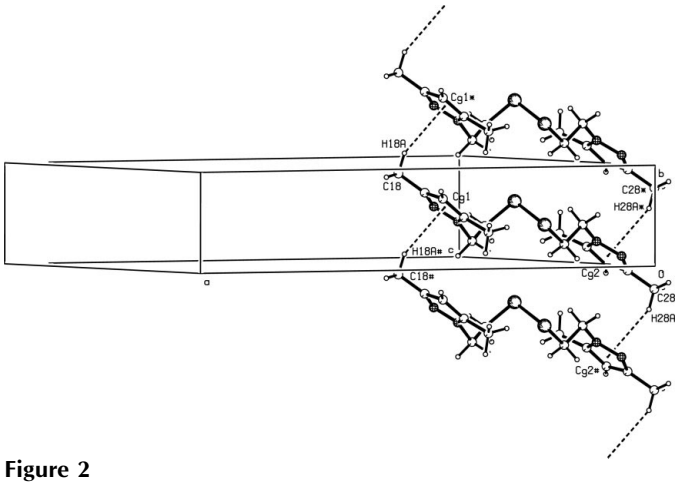



**Figure 2**
Part of the crystal structure of (I), showing a chain of molecules linked by C—H···$\pi$(pyrazole) interactions that propagate along the *b* axis. Atoms labelled with an asterisk (*) or hash (#) occupy the symmetry positions ($x$, $1 + y$, $z$) or ($x$, $y - 1$, $z$), respectively. *Cg*1 and *Cg*2 are the centroids of the N11–C15 and N21–C25 pyrazole rings, respectively.

pyrazole moieties in (I) are chemically equivalent, they are not related by any (approximate) symmetry operation.

The geometric details of the intermolecular contacts that determine the supramolecular structure of (I) are presented in Table 2. The molecular conformation of the disulfide molecules allows them to stack such that one methyl group of each 3,5-dimethylpyrazole ring is placed directly above, or below, one of the pyrazole rings of the adjacent translation-related molecules [C18—$Cg1^{i}$ = 3.757 (2) Å and C28—$Cg2^{ii}$ = 3.791 (2) Å; *Cg*1 and *Cg*2 are the centroids of the N11—C15 and N21—C25 pyrazole rings, respectively; symmetry codes: (i) $x$, $1 + y$, $z$; (ii) $x$, $y - 1$, $z$]. As shown in Fig. 2, weak, yet directional, C—H···$\pi$(pyrazole) interactions link the molecules into chains that run along the *b* direction. Similar interactions have been described for several pyrazole structures (Glidewell *et al.*, 2002). An additional weak intermolecular C27—H27*B*···$S1^{ii}$ hydrogen bond occurs within the chains.

## Experimental

The title compound was obtained as a by-product in the synthesis of $[Ni(etdmp)_2]$ [Hetdmp is 1-(2-sulfanylethyl)-3,5-dimethylpyrazole]. The Hetdmp ligand was prepared as described in the literature (Bouwman & Reedijk, 1998). Reaction of Hetdmp with anhydrous $[Ni(acac)_2]$ (acac is acetylacetonate) in toluene produced the mononuclear complex $[Ni(etdmp)_2]$ in 60% yield. Attempted recrystallization of the complex from a toluene/hexane mixture led instead, after several weeks, to the isolation of colourless needles of the disulfide byproduct bis[(3,5-dimethylpyrazol-1-yl)ethyl] disulfide, (I), that were suitable for X-ray analysis. The disulfide, which crystallizes slowly from the crude ligand oil when it is stored in air, has been characterized previously by $^{1}$H and $^{13}$C NMR (Bouwman & Reedijk, 1998).

*Crystal data*

| | |
|---|---|
| $C_{14}H_{22}N_4S_2$ | $D_x$ = 1.273 Mg m$^{-3}$ |
| $M_r$ = 310.48 | Mo $K\alpha$ radiation |
| Monoclinic, $C2/c$ | Cell parameters from 15586 reflections |
| $a$ = 28.5692 (4) Å | $\theta$ = 1.0–27.5° |
| $b$ = 4.6529 (1) Å | $\mu$ = 0.33 mm$^{-1}$ |
| $c$ = 26.4989 (4) Å | $T$ = 150 (2) K |
| $\beta$ = 113.137 (1)° | Needle, colourless |
| $V$ = 3239.17 (10) Å$^3$ | 0.69 × 0.15 × 0.12 mm |
| $Z$ = 8 | |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer | $R_{int}$ = 0.092 |
| $\varphi$ and $\omega$ scans | $\theta_{max}$ = 27.5° |
| Absorption correction: none | $h = -36 \rightarrow 36$ |
| 16592 measured reflections | $k = -6 \rightarrow 5$ |
| 3686 independent reflections | $l = -34 \rightarrow 34$ |
| 2856 reflections with $I > 2\sigma(I)$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 1.361P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)]$ = 0.039 | $(\Delta/\sigma)_{max}$ = 0.001 |
| $wR(F^2)$ = 0.101 | $\Delta\rho_{max}$ = 0.31 e Å$^{-3}$ |
| $S$ = 1.02 | $\Delta\rho_{min}$ = −0.32 e Å$^{-3}$ |
| 3686 reflections | |
| 185 parameters | |
| H-atom parameters constrained | |

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

| | | | |
|---|---|---|---|
| S1—C17 | 1.8156 (16) | S2—C27 | 1.8097 (15) |
| S1—S2 | 2.0396 (6) | | |
| C17—S1—S2 | 105.73 (6) | C27—S2—S1 | 103.95 (6) |
| N11—C16—C17—S1 | 65.69 (16) | N21—C26—C27—S2 | −176.75 (10) |
| S2—S1—C17—C16 | 54.12 (12) | S1—S2—C27—C26 | 68.12 (12) |
| C17—S1—S2—C27 | 81.87 (8) | | |

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

*Cg*1 and *Cg*2 are the centroids of the N11–C15 and N21–C25 pyrazole rings, respectively

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C18—H18*A*···$Cg1^{i}$ | 0.98 | 2.84 | 3.757 (2) | 156 |
| C28—H28*A*···$Cg2^{ii}$ | 0.98 | 2.90 | 3.791 (2) | 151 |
| C27—H27*B*···$S1^{ii}$ | 0.99 | 2.83 | 3.5233 (17) | 127 |

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

The maximum crystal dimension (0.69 mm) of the crystal analysed is somewhat large because the long needles of (I) could not be cut without breaking. The pyrazole and methylene H atoms were placed in idealized positions and allowed to ride on their C atoms, with C—H

= 0.95 or 0.99 Å, respectively, and $U_{iso}(H) = 1.2U_{eq}(C)$. The methyl H atoms were constrained to idealized geometries and allowed to rotate freely about their C—C bonds, with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL*2000 (Otwinowski & Minor, 1997); data reduction: *HKL*2000; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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