

within 0.10 Å. The orientation of the PEt₃ ligand with respect to the Pd coordination plane, with Cl(1)–Pd–P–C(21) = –9.8 (3) and Pd–P–C(21)–C(22) = 171.0 (6)°, resembles closely those found in *trans*-Pt^{II}Cl₂(PEt₃) species (e.g. Manojlović-Muir & Muir, 1974*b*) but does not seem to have been described previously for Pd^{II}.

The bonds radiating from the sulfimide N(2) atom deviate slightly from planarity, N(2) lying 0.143 (4) Å from the PdSC(3) plane. The N(2)–S and N(2)–C(3) bonds are roughly normal to the Pd coordination plane [Cl(1)–Pd–N(2)–S = –86.8 (3), Cl(1)–Pd–N(2)–C(3) = 75.3 (3)°]. The N(2)–S distance [1.638 (4) Å] is consistent with some multiple-bond character. This bond nearly eclipses C(3)–N(1) [S–N(2)–C(3)–N(1) = 9.3 (4)°]. The C(3)–N(2)–S–X torsion angles are –91.7 (4) and 164.2 (4)° for X = C(1) and C(2), respectively. The N(2)–S and N(2)–C(3) bond lengths, the torsion angles across these bonds and the S–N(2)–C(3) bond angle are in excellent agreement with corresponding values in the uncomplexed sulfimides Me₂S=N–C₆H₄X, X = *m*- or *p*-NO₂ (Cameron, Freer & Maltz, 1981). Evidently the Pd atom has little effect on the bonding or conformation of the sulfimide ligand. This conformation is such that the lone pairs on S and N(1) both point away from the Pd atom, the S...N(1) intramolecular distance [2.665 (4) Å] being notably short. Finally, Cameron *et al.* (1981) have shown that

the protonated sulfimide cation, (Me₂S=NH–C₆H₄–Cl-*p*)⁺, adopts a different conformation from those of the unprotonated sulfimide molecules or from that of the Pd complex, even though the site of protonation, like that of metallation, is the imide-N atom.

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The Structure of *cis,trans,cis*-Diaquabis(5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine-*N*³)-bis(thiocyanato-*N*)iron(II)

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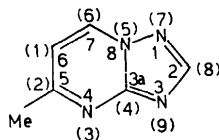
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Abstract. C₁₄H₁₆FeN₁₀O₂S₂, *M_r* = 476.31, monoclinic, *C*2/*c*, *a* = 15.765 (5), *b* = 7.909 (2), *c* = 16.211 (7) Å, β = 94.68 (3)°, *V* = 2015 (1) Å³, *Z* = 4, *D_m* = 1.55, *D_x* = 1.57 Mg m⁻³, Mo *K*α, λ̄ = 0.71069 Å, μ = 0.979 mm⁻¹, *F*(000) = 976, room temperature, *R* = 0.036, *wR* = 0.042, 1088 independent observed reflections. The structure consists of Fe²⁺ ions pseudo-octahedrally coordinated by two water

molecules (*cis*), two N-bonding thiocyanate groups (*cis*) and two N₃-coordinating 5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine (C₆H₆N₄) ligands (*trans*). The Fe–O(water) bonds are 2.156 (5) Å, the Fe–N(thiocyanate group) bonds are 2.109 (5) Å and the Fe–N(organic ligand) bonds are 2.225 (5) Å. The organic ligands are associated, by stacking interactions, in pairs arranged in chains running along the [011] direction.

Introduction. Azapurines, containing the 1,2,4-triazole ring, are known to be versatile ligands for several kinds of metals (Dillen, Lenstra, Haasnoot & Reedijk, 1983). Because of methyl substitution in the six-membered ring the ligand 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine (abbreviated as dmtp) is mainly N₃ coordinated (IUPAC numbering, see below) (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1983, 1984, 1985; Biagini Cingi, Manotti Lanfredi, Tiripicchio, Reedijk & Haasnoot, 1986). Removal of the methyl groups produces the unsubstituted ligand (tp), for which an N₁,N₃ bidentate bridging coordination mode has been found (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Cornelissen, Haasnoot & Reedijk, 1986), resulting in a two-dimensional layered system. We wondered whether the monosubstituted 5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine (abbreviated mtp) would behave as a monodentate (like dmtp) or as a bidentate ligand (like tp). It turned out, however, that this ligand behaves like dmtp and not tp. We report the crystal structure of the compound [Fe(NCS)₂(mtp)₂(H₂O)₂] which is comparable to that of [Cd(NCS)₂(dmtp)₂(H₂O)₂] (Dillen, Lenstra, Haasnoot & Reedijk, 1983).

A scheme of the 5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine (mtp) ligand showing IUPAC systematic numbering of ring atoms (inside) and biochemical numbering (parentheses), used in the structure determination, is shown below.



Experimental. The ligand mtp was prepared according to a known procedure (Allen, Beilfuss, Burness, Reynolds, Tinker & Van Allan, 1959). Crystals of the title compound were grown from a solution of FeSO₄ (2 mmol) in water (10 ml) after addition of a solution of NH₄NCS (4 mmol) and mtp (4 mmol) in water (10 ml). *D_m* by flotation.

Prismatic crystal, approximate dimensions 0.20 × 0.25 × 0.35 mm, used for X-ray analysis; Siemens AED diffractometer, Nb-filtered Mo *K*α radiation; 24 reflections for lattice-parameter measurements, 10.5 < θ < 15.2°; 1845 independent reflections with 3 < θ < 25°, -20 ≤ *h* ≤ 20, 0 ≤ *k* ≤ 10, 0 ≤ *l* ≤ 19, 1088 with *I* > 2σ(*I*); no significant intensity deterioration of one standard reflection (242). Lp correction, absorption ignored. Patterson and Fourier methods; full-matrix least-squares refinement, anisotropic for non-H atoms (SHELX76; Sheldrick, 1976); H localized directly from Δ*F* synthesis, isotropically refined; ∑*w*|Δ*F*|² minimized; final *R* = 0.036 and *wR* = 0.042, unit weights; (Δ/σ)_{max} = 0.85, final Δρ excursion ≤ |0.9| e Å⁻³; atomic scattering factors (anomalous

Table 1. Fractional atomic coordinates (×10⁴) and equivalent isotropic thermal parameters for the non-H atoms, with *e.s.d.*'s in parentheses

	$B_{\text{eq}} = \frac{1}{3}\pi^2\text{trace } \bar{U}$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Fe	0	1661 (2)	2500	2.58 (3)
S	-2229 (1)	-2623 (2)	2139 (1)	4.83 (5)
Ow	917 (3)	3661 (6)	2738 (3)	3.99 (12)
N	-966 (3)	-172 (7)	2296 (3)	3.63 (14)
N(3)	-935 (3)	3362 (7)	525 (3)	3.40 (12)
N(5)	203 (3)	2228 (6)	-167 (3)	3.31 (13)
N(7)	938 (3)	1342 (7)	23 (3)	4.20 (16)
N(9)	262 (3)	1855 (6)	1175 (3)	2.95 (12)
C	-1503 (3)	-1173 (7)	2224 (3)	2.93 (16)
C(1)	-865 (5)	3611 (9)	-934 (4)	4.37 (22)
C(2)	-1271 (4)	3897 (8)	-205 (4)	3.67 (17)
C(4)	-198 (3)	2527 (7)	534 (3)	2.78 (15)
C(6)	-134 (5)	2786 (9)	-913 (4)	4.43 (21)
C(8)	928 (4)	1163 (8)	825 (4)	3.41 (16)
C(10)	-2101 (5)	4811 (12)	-231 (6)	5.50 (24)

dispersion of Fe atom) from *International Tables for X-ray Crystallography* (1974); calculations performed on the Cyber computer of the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale, Casalecchio (Bologna), with financial support from the University of Parma.*

Discussion. The atomic coordinates for the non-H atoms are given in Table 1. Relevant bond distances and angles are given in Table 2.

The structure consists of discrete *trans*-(mtp-*N*),-*cis*-(thiocyanato-*N*),*cis*-(OH₂) octahedral Fe^{II} complexes, having an imposed C₂ symmetry (see Fig. 1). The Fe-N bond lengths involving N atoms from NCS groups and mtp molecules are 2.109 (5) and 2.225 (5) Å respectively, and Fe-O are 2.156 (5) Å. These agree with those observed for octahedrally coordinated Fe complexes with isothiocyanate, dmtp and water ligands (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1985). Thus, the mtp molecule shows the same ligand behaviour as dmtp.

The crystal packing is shown in Fig. 2. Both intramolecular H bonds, involving coordinated water molecules and non-bridgehead pyrimidine N atoms from organic ligands (which determine an indirect chelation of the latter), and intermolecular H bonds between water molecules and thiocyanate S atoms from different complexes are present. The mtp ligands are associated in pairs, through the symmetry centres at 0,0,0 and 0,½,½ with interplanar distance 3.290 (3) Å; the pairs form chains running along the [011] direction, the interplanar separation between parallel mtp molecules from different chains being 3.515 (3) Å.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42994 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Principal bond distances (Å) and angles (°)

(i) In the coordination polyhedron of the Fe atom

Fe—N	2.109 (5)	Fe—O _w	2.156 (5)
Fe—N(9)	2.225 (5)		

N—Fe—O _w ⁱ	90.6 (2)	O _w —Fe—N(9)	87.0 (2)
N—Fe—O _w	175.8 (2)	N(9)—Fe—O _w ⁱ	87.2 (2)
N—Fe—N ⁱ	93.1 (2)	N(9)—Fe—N ⁱ	90.6 (2)
O _w —Fe—O _w ⁱ	85.6 (2)	N(9)—Fe—N	94.8 (2)

(ii) In the thiocyanate ligand

N—C	1.158 (7)	C—S	1.618 (5)
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N—C—S	177.9 (5)	C—N—Fe	176.7 (5)
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(iii) In the organic ligand

C(1)—C(2)	1.407 (9)	N(5)—N(7)	1.368 (7)
C(2)—N(3)	1.326 (8)	N(7)—C(8)	1.309 (8)
N(3)—C(4)	1.335 (7)	C(8)—N(9)	1.349 (8)
C(4)—N(5)	1.365 (7)	N(9)—C(4)	1.329 (7)
N(5)—C(6)	1.354 (8)	C(2)—C(10)	1.492 (10)
C(6)—C(1)	1.322 (11)		

C(2)—C(1)—C(6)	120.8 (6)	N(9)—C(4)—N(5)	108.7 (4)
C(1)—C(2)—N(3)	121.5 (6)	C(4)—N(5)—N(7)	110.0 (4)
C(2)—N(3)—C(4)	116.8 (5)	N(5)—N(7)—C(8)	101.6 (5)
N(3)—C(4)—N(5)	122.5 (5)	N(7)—C(8)—N(9)	116.5 (6)
C(4)—N(5)—C(6)	120.8 (5)	C(8)—N(9)—C(4)	103.1 (5)
N(5)—C(6)—C(1)	117.5 (6)	C(4)—N(9)—Fe	130.5 (4)
C(1)—C(2)—C(10)	120.8 (6)	C(8)—N(9)—Fe	126.1 (4)
N(3)—C(2)—C(10)	117.7 (6)		

(iv) H bonds

O _w ...N(3 ⁱ)	2.824 (7)	O _w —H(1 _w)—N(3 ⁱ)	148 (6)
H(1 _w)...N(3 ⁱ)	2.04 (7)		

O _w ...S ⁱⁱ	3.314 (5)	O—H(2 _w)—S ⁱⁱ	157 (5)
H(2 _w)...S ⁱⁱ	2.46 (6)		

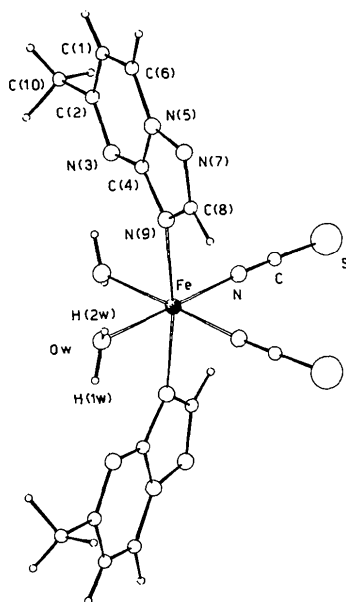
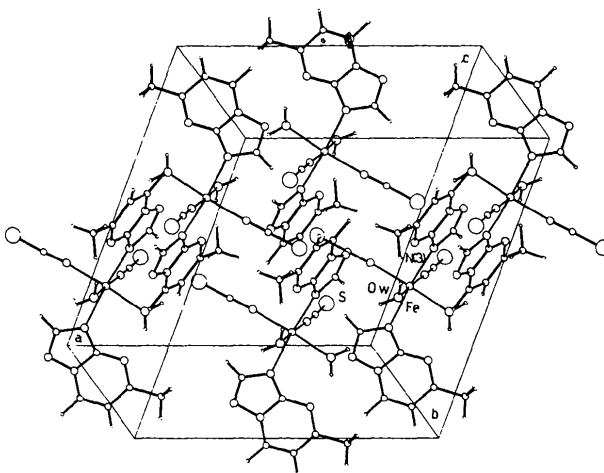
Symmetry code: (i) $-x, y, \frac{1}{2}-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}+y, z$.Fig. 1. View of the [Fe(NCS)₂(mtp)₂(H₂O)₂] complex with the atomic numbering scheme.

Fig. 2. Packing of the complexes.

The structure of this mtp-Fe^{II} complex is very similar to that of the dmtp-Cd^{II} compound, [Cd(NCS)₂(dmtp)₂(H₂O)₂] (Dillen, Lenstra, Haasnoot & Reedijk, 1983), where Cd^{II} is octahedrally coordinated by two N-bonded (*trans* oriented) dmtp molecules, two water molecules (*cis*) and two N-bonded NCS groups. Neither the increase of the ionic radius from Fe²⁺ to Cd²⁺ nor the larger steric demand of dmtp compared to mtp modifies substantially the configuration of the complexes and their reciprocal linkage.

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