

As observed in [Co(pnao-H)(NO₂)₂] (Murmman & Schlemper, 1973) and [Co(pnao-H)(OREO₃)] (Liss & Schlemper, 1975), the Cu–N(amine) distances [2.049, 2.037 (3) Å] are longer than the Cu–N(oxime) distances [1.977, 1.979 (3) Å], suggesting a stronger Cu–N(oxime) bond. At least part of this difference can be attributed to the usual shortening of 0.03–0.04 Å on change of hybridization from *sp*³ to *sp*² for the N atom. The reason for the rest of the shortening is not clear.

The intramolecular hydrogen bond has an O···O distance of 2.475 (4) Å which compares well with the value of 2.46 (2) Å in the ReO₄⁻ complex. Thus, shifting the Cu atom away from the N₄ plane does not facilitate a shortening of the O···O distance. Both of these are significantly longer than the 2.432 (3) Å in [Co(pnao-H)(NO₂)₂]. All of the other bond distances and angles are in reasonable agreement with those of the perrhenate structure. Thus the strong CN⁻ coordination to the Cu^{II} atom has little effect on the ligand geometry: its main effect is displacing the metal from the plane of the organic ligand.

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The Structure of *poly-Bis(thiocyanato-N)bis-μ-(1,2,4-triazole-N²,N⁴)-iron(II)**

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Abstract. [Fe(C₂H₃N₃)₂(NCS)₂], C₆H₆FeN₈S₂, *M_r* = 310.0, orthorhombic, *a* = 7.882 (1), *b* = 16.312 (4), *c* = 9.890 (2) Å, *Z* = 4, *D_c* = 1.620 Mg m⁻³; *R* = 0.037 (*R_w* = 0.048) for 963 independent reflexions. The compound is isomorphous with [Co^{II}(C₂H₃N₃)₂(NCS)₂].

Introduction. Very recently, we reported the crystal structures of [*M*^{II}(trz)₂(NCS)₂] with *M* = Co, Zn, Cu and trz = 1,2,4-triazole (Engelfriet, den Brinker, Verschoor & Gorter, 1979). Although crystallizing in different space groups, the three compounds exhibit the

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same basic features: two-dimensional *M*^{II} networks with 2,4-bridging trz molecules and NCS⁻ groups, acting as N donors, on either side of the planes. From X-ray powder diffraction the Mn, Fe, Co and β-Ni members of the series were found to be isomorphous (Haasnoot & Groeneveld, 1977). Nevertheless, there were several reasons for examining a single crystal of the Fe compound as well: the Mössbauer spectrum of this compound showed a quadrupole doublet with strongly broadened lines, while for a proper refinement of the neutron powder diffraction pattern precise values of the positional parameters are needed (Engelfriet, Groeneveld & Nap, 1980). Single crystals were prepared in the following way. A solution of FeCl₂·4H₂O, slightly acidified with HCl, was added to a solution containing equimolar quantities of trz and

* 1,2,4-Triazole Complexes. XI. Part X: Donker, Haasnoot & Groeneveld (1980).

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NH₄NCS. The concentration of [Fe(trz)₂(NCS)₂] was approximately 0.1 mmol ml⁻¹. SO₂ was passed through the brownish solution to remove ferric ions. A beaker containing the solution was placed over P₂O₅ in a desiccator which was flushed with N₂. After 1–2 weeks very pale green crystals appeared which were quickly removed and dried with filter paper. The crystals are diamond shaped, though the diamonds are often elongated to parallelograms.

A crystal of dimensions 0.21 × 0.45 × 0.50 mm was mounted on an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Mo K α radiation was used for determining the unit-cell parameters and the space group and for measuring the reflexion intensities [μ (Mo K α) = 1.491 mm⁻¹]. The data were corrected for Lorentz and polarization effects and for absorption (de Graaff, 1973). 2384 reflexions were measured, 1266 of which were independent. 963 independent reflexions had intensities greater than twice their standard deviations (calculated from counting statistics, with corrections for inaccuracies of the attenuation factor and absorption).

Calculations were carried out on the Leiden University IBM 370-158 computers, using a set of programs written or modified by Dr R. A. G. de Graaff and Mrs E. W. Rutten-Keulemans. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The function minimized in the least-squares refinement was $\sum w(\Delta F)^2$ with $\Delta F = |F_o| - |F_c|$ and $w = \sigma_F^{-2}$. Discrepancy indices are defined as $R = \sum |\Delta F| / \sum |F_o|$ and $R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$.

In view of the expected similarity with the structure of [Co(trz)₂(NCS)₂], the positional and thermal parameters obtained for that compound (Engelfriet *et al.*, 1979) were used as starting parameters. It should be mentioned first that for the Co compound refinement in *Aba2* resulted in a distorted trz ring geometry compared with the trz rings in the Zn and Cu compounds and in uncoordinated trz. Furthermore, the parameters of the N(1) and C(5) and the N(2) and N(4) atoms were strongly correlated. It was assumed that these results were due to disorder in the orientations of the trz groups. A satisfactory result (with a

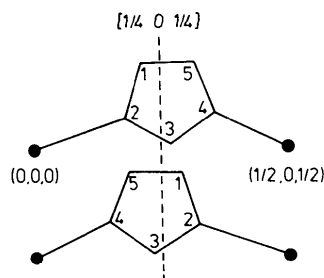


Fig. 1. Alternative positions of the trz rings (slightly exaggerated). The numbering of the ring atoms is the same as in Figs. 2 and 3.

Table 1. Fractional coordinates and isotropic temperature factors (\AA^2) for [Fe(trz)₂(NCS)₂]

	x	y	z	B_{eq}^*
Fe	0	0	0	1.94 (3)
S	0.4333 (1)	-0.2068 (1)	-0.014 (1)	4.8 (4)
C	0.2634 (3)	-0.1491 (2)	-0.011 (4)	2.5 (11)
N	0.1443 (2)	-0.1089 (2)	0.012 (3)	2.6 (1)
N(1)	0.195 (2)	0.1247 (4)	0.204 (2)	2.9 (6)
N(2)	0.166 (2)	0.0461 (7)	0.168 (2)	2.3 (4)
C(3)	0.256 (3)	0.0049 (2)	0.256 (3)	3.1 (5)
N(4)	0.337 (2)	0.0514 (8)	0.348 (2)	2.7 (5)
C(5)	0.296 (2)	0.1266 (5)	0.312 (2)	2.8 (5)
H(1)†	0.1451	0.1764	0.1550	
H(2)†	0.2642	-0.0532	0.2546	6.8 (7)
H(3)†	0.3332	0.1751	0.3561	

* $B_{eq} = \frac{1}{3} \pi^2 \text{trace } \bar{U}$.

† Calculated positions.

significantly lower *R* factor) was obtained by imposing slack constraints (Waser, 1963) on the trz rings and refinement in *Abam*. Thus, the disorder was accounted for by introducing an inversion centre which implies that 50% of the rings are inverted. The two alternative positions are visualized in Fig. 1.

At first we used the Co parameters, without disorder. Refinement in *Aba2* gave the same result as in the Co compound: deformed trz rings and strong correlations between the parameters of the N(2) and N(4) and the N(1) and C(5) atoms. We assumed that these results again are attributable to the presence of disordered trz rings. Therefore, we proceeded as in the Co compound and imposed slack constraints (Waser, 1963) on the trz rings, placing the H atoms at calculated positions. As constraints we used the values for bond lengths and angles found in the refinement of the Zn compound (Engelfriet *et al.*, 1979). By introducing an inversion centre, thus accounting for 50% disorder, $R = 0.038$ ($R_w = 0.052$) was obtained. It must be noted, however, that the introduction of an inversion centre implies 50% disorder in the NCS groups as well. Further, there is no reason why the degree of disorder should be exactly 50%. Therefore, in the last cycles we refined the occupation rates of the inverted trz groups and, independently, those of the NCS groups. It turned out that the occupation rates of the inverted trz and NCS groups did not differ significantly. After a correction for extinction had been applied, we obtained $R = 0.037$ ($R_w = 0.048$), with an occupation rate of 40 (1)% for the inverted (enantiomorphous) structure.

Positional parameters are listed in Table 1.*

Discussion. Relevant distances and angles with their e.s.d.'s are given in Table 2. The structure is shown in

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35601 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Distances (Å) and angles (°) in [Fe(trz)₂(NCS)₂]

Fe—N(2)	2.24 (2)	N(2)—Fe—N(2) ⁱⁱ	84.5 (8)
Fe—N(4) ⁱ	2.15 (2)	N(4)—Fe—N(4) ⁱⁱ	91.1 (9)
Fe—N	2.112 (3)	N—Fe—N ⁱⁱⁱ	174 (2)
N—C	1.167 (5)	N—Fe—N(2)	85.9 (7)
C—S	1.636 (3)	N—Fe—N(2) ⁱⁱ	89.5 (7)
S—C(5) ^{iv}	3.40 (2)	N—Fe—N(4) ⁱ	92.6 (7)
S—N(1) ^v	3.54 (2)*	N—Fe—N(4) ⁱⁱⁱ	91.8 (7)
S—N(1) ^v	3.64 (1)	N(2)—Fe—N(4) ⁱ	92.3 (6)
S—H(5) ^{iv}	3.48 (1)*	N(2)—Fe—N(4) ⁱⁱⁱ	176.0 (5)
S—H(1) ^v	2.45 (2)	Fe—N—C	154 (2)
S—H(1) ^v	2.60 (2)*	N—C—S	170 (4)
S—H(1) ^v	2.61 (2)	C—S—H(1) ^v	102 (1)
S—H(1) ^v	2.44 (1)*	S—H(1) ^v —N(1) ^v	167 (2)
		C—S—H(5) ^{iv}	101 (1)
trz ring		S—H(5) ^{iv} —C(5) ^{iv}	176 (2)
N(1)—N(2)	1.35 (1)	H(1) ^v —S—H(5) ^{iv}	71.6 (5)
N(2)—C(3)	1.31 (3)		
C(3)—N(4)	1.34 (3)	trz ring	
N(4)—C(5)	1.32 (2)	N(1)—N(2)—C(3)	103 (1)
C(5)—N(1)	1.33 (3)	N(2)—C(3)—N(4)	114.6 (9)
H(1)—N(1)	1.05†	C(3)—N(4)—C(5)	103 (2)
H(3)—C(3)	0.95†	N(4)—C(5)—N(1)	110 (1)
H(5)—C(5)	0.95†	C(5)—N(1)—N(2)	110 (1)

Symmetry code: (i) $\frac{1}{2} - x, y, z - \frac{1}{2}$; (ii) \bar{x}, \bar{y}, z ; (iii) $x - \frac{1}{2}, \bar{y}, z - \frac{1}{2}$; (iv) $x, y - \frac{1}{2}, z - \frac{1}{2}$; (v) $\frac{1}{2} - x, \bar{y} - \frac{1}{2}, z$.

* Distances with the trz ring at alternative (inverted) positions calculated with the S atom at x, y, \bar{z} .

† H atoms in calculated positions.

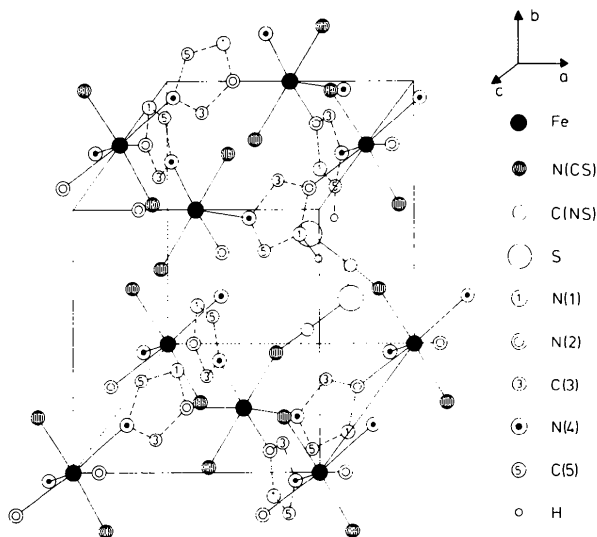


Fig. 2. FIGATOM drawing (Langlet, 1972) of the structure of [Fe(trz)₂(NCS)₂]. For clarity only two NCS groups and two H atoms are shown. Possible interlayer hydrogen bonding is indicated by dotted lines.

Fig. 2, neglecting disorder. Fig. 3 presents a (101) section of the structure and gives the numbering scheme.

The structure is practically identical to that of the corresponding Co compound (Engelfriet *et al.*, 1979).

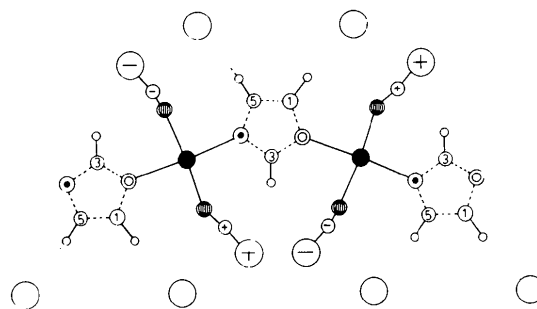


Fig. 3. (101) section of [Fe(trz)₂(NCS)₂]. Atom symbols are the same as in Fig. 2. The atoms shown are within 1 Å of the plane of the drawing, except for C and S atoms marked + or -. C(+) and S(+) are at 1.558 and 2.584 Å above and C(-) and S(-) are at 1.690 and 2.756 Å below the plane of the drawing.

The Fe^{II} ions occupy the special positions (0,0,0) and (0, $\frac{1}{2}$, $\frac{1}{2}$). They are connected by 2,4-coordinating trz groups in the planes $y = 0$ and $y = \frac{1}{2}$ and thus a two-dimensional layered structure is formed. N-donating NCS⁻ groups are on either side of the planes. The somewhat distorted FeN₆ octahedra are tilted in the planes $z = 0$ and $z = \frac{1}{2}$. The angle between the (SC)N—Fe—N(CS) axis and the *b* direction is approximately 31°.

The trz molecules are quite planar (see Table 3) and are almost parallel to the *b* axis. The distances and angles mentioned in Table 2 do not differ significantly from those found in [Co(trz)₂(NCS)₂], with the exception of the *M*—N distances in the FeN₆ octahedra which are about 0.04 Å longer than those in the CoN₆ octahedra. As in the Co, Zn and Cu complexes, the H(1)⋯S and H(5)⋯S distances are indicative of interlayer hydrogen bonding. As regards the disordered trz rings, it is plausible to consider two possibilities: (i) the two enantiomorphs are in separate domains, or (ii) the orientations of the trz rings are randomly distributed throughout the structure. In the case of (i) there would be only one type of FeN₆ octahedra, whereas (ii) would result in several slightly different FeN₆ octahedra. Because the existence of different Fe sites is

Table 3. Distances (Å) from the ring atoms and the coordinating metal atoms to the least-squares plane (of the non-hydrogen atoms) of the triazole ring in [Fe(trz)₂(NCS)₂]

The numbers of the H and metal atoms are those of the atoms to which they are attached. The equation of the plane in direct space is $-0.7961X - 0.0380Y + 0.6040Z + 0.0743 = 0$.

N(1)	-0.006 (5)	Fe(2)	0.074 (2)
N(2)	0.009 (2)	Fe(4)	-0.076 (2)
C(3)	-0.009 (2)	H(1)*	-0.020
N(4)	0.005 (2)	H(3)*	-0.029
C(5)	0.001 (2)	H(5)*	0.002

* Calculated positions.

the most acceptable explanation for the line-broadening in the Mössbauer quadrupole doublet already mentioned, the measurements are clearly in favour of possibility (ii).

To verify this, we also performed Mössbauer measurements on $[\text{Zn}(\text{trz})_2(\text{NCS})_2]$ doped with approximately 0.1% ^{57}Fe . The Zn compound does not show disorder and although it crystallizes in a different space group (*Pbcn*), the site symmetries of the metal ions are the same in both compounds. Despite the poor statistics of the spectrum, no significant line-broadening was observed. The above results justify the conclusion that the trz rings are orientated in a random way.

No evidence for disorder, such as streaks or diffuse reflections, could be observed in X-ray photographs. This may be due to the high background level, caused by the Cu $K\alpha$ radiation used.

Finally we mention that, because the degree of disorder in $[\text{Fe}(\text{trz})_2(\text{NCS})_2]$ differs significantly from 50%, we have re-examined our results on the corresponding Co compound. In a previous paper (Engel-

friet *et al.*, 1979) we assumed the degree of disorder in the Co compound to be 50%. The occupation rate of one of the enantiomorphs was found to be 42 (1)%. However, refinement of all parameters together with the occupation rate did not produce significant changes in the *R* factors and the positional parameters.

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Structure of *trans*-Difluoro{[7*R*(*S*),14*S*(*R*)]-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}nickel(II) Pentahydrate

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Abstract. $[\text{Ni}(\text{C}_{16}\text{H}_{36}\text{N}_4)\text{F}_2] \cdot 5\text{H}_2\text{O}$, triclinic, $P\bar{1}$, $a = 11.185$ (2), $b = 13.364$ (3), $c = 8.890$ (1) Å, $\alpha = 83.17$ (2), $\beta = 104.94$ (1), $\gamma = 113.00$ (1)°, $U = 1181.6$ (4) Å³, $Z = 2$, $D_m = 1.32_9$, $D_x = 1.32_5$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.870$ mm⁻¹; $R = 0.031$ and $R_w = 0.039$ for 5958 independent reflexions. The Ni^{II} ion is surrounded pseudo-octahedrally by four N atoms of the macrocyclic ligand in a single plane and by two F⁻ ions occupying the axial positions. The dispositions of water molecules around the Ni^{II} ion are discussed.

Introduction. This is part of a series of structural investigations on the Ni^{II} halide complexes containing the title macrocyclic ligand, hereafter abbreviated as *meso*-Me₆[14]aneN₄. A main feature of interest in these studies is a clarification of the dispositions of water molecules around a Ni^{II} ion and thereby to explain the role played by water in the spin-state variations among the Ni^{II} complexes. The crystal structures of the two

complexes formed with NiCl₂ and the title ligand, which are the low-spin four-coordinate complex $[\text{Ni}(\textit{meso}\text{-Me}_6[14]\text{aneN}_4)\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ and the high-spin six-coordinate complex $[\text{NiCl}_2(\textit{meso}\text{-Me}_6[14]\text{aneN}_4)] \cdot 2\text{CHCl}_3$, have been reported (Ito & Toriumi, 1981). In this paper the structure of the title complex $[\text{NiF}_2(\textit{meso}\text{-Me}_6[14]\text{aneN}_4)] \cdot 5\text{H}_2\text{O}$ is described. The compound was prepared from the corresponding perchlorate salt $[\text{Ni}(\textit{meso}\text{-Me}_6[14]\text{aneN}_4)](\text{ClO}_4)_2$ (Warner & Busch, 1969) by ion exchange (Dowex 1X8). Slow evaporation of the eluate from the column yielded triclinic single crystals. A pale-violet plate was shaped into an approximate sphere with a diameter of 0.40 mm. X-ray diffraction data were measured on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Within the range $2\theta \leq 60^\circ$, 5958 independent reflexions with $|F_o| \geq 3\sigma(|F_o|)$ were obtained. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied.