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#### Key indicators

Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.014 \text{ \AA}$   
Disorder in main residue  
R factor = 0.057  
wR factor = 0.144  
Data-to-parameter ratio = 15.0

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

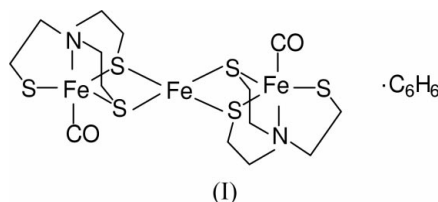
## $\mu$ -Ferrio-bis{carbonyl[ $\mu$ -2,2',2''-nitrilo- triethanethiolato(3-)-N,S,S',S'':S,S']iron(II)} benzene solvate

The neutral title complex,  $[\{\text{Fe}(\{\text{SCH}_2\text{CH}_2\}_3\text{N})(\text{CO})-\text{S},\text{S}'\}_2(\mu\text{-Fe})]\cdot\text{C}_6\text{H}_6$  or  $[\text{Fe}_3(\text{C}_6\text{H}_{12}\text{NS}_3)_2(\text{CO})_2]\cdot\text{C}_6\text{H}_6$ , contains two trigonal bipyramidally coordinated  $\text{Fe}^{\text{II}}$  atoms bridged by a tetrahedral  $\text{Fe}^{\text{II}}$  atom. There is disorder in one  $\{\text{SCH}_2\text{CH}_2\}_3\text{N}$  ligand and in the solvent benzene present in the crystal structure. Dimensions in the complex are comparable to those in other five-coordinate metal- $(\{\text{SCH}_2\text{CH}_2\}_3\text{N})$  complexes.

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#### Comment

The title compound, (I), was isolated as a minor product from an attempted synthesis of a novel nickel-iron-thiolate complex with features similar to some of those of the active sites of the enzymes NiFe-hydrogenase, nickel carbon monoxide dehydrogenase and acetyl-CoA synthase (Evans, 2001). The same compound,  $[\{\text{Fe}(\{\text{SCH}_2\text{CH}_2\}_3\text{N})(\text{CO})-\text{S},\text{S}'\}_2(\mu\text{-Fe})]$ , but unsolvated (Davies *et al.*, 2000), and other trinuclear compounds  $[\{\text{Fe}(\{\text{SCH}_2\text{CH}_2\}_3\text{N})(\text{CO})-\text{S},\text{S}'\}_2(\mu\text{-M})]$  [ $M = \text{Co}, \text{V}$  (Davies *et al.*, 2000);  $M = \text{Ni}$  (Smith *et al.*, 2001)], have been reported previously.



The X-ray analysis of  $[\{\text{Fe}(\{\text{SCH}_2\text{CH}_2\}_3\text{N})(\text{CO})-\text{S},\text{S}'\}_2(\mu\text{-Fe})]\cdot\text{C}_6\text{H}_6$  shows two  $\text{Fe}(\{\text{SCH}_2\text{CH}_2\}_3\text{N})(\text{CO})$  units linked through a third Fe atom, resulting in two iron environments, which are confirmed by Mössbauer spectra. In each of the outer units the Fe atom is trigonal bipyramidally coordinated to one CO and by one  $\{\text{SCH}_2\text{CH}_2\}_3\text{N}$  ligand, with the Fe atoms displaced 0.0702 (13) and 0.0801 (13) Å out of the  $\text{S}_3$  equatorial planes, towards the CO ligands. The normals to the two  $\text{S}_3$  planes are tilted with respect to each other by 90.3°.

The central Fe atom is tetrahedrally coordinated by four S atoms, with angles about the Fe lying in the range 105.37 (11) to 116.63 (11)° and an average  $\text{Fe}\cdots\text{Fe}$  distance to the outer Fe atoms of 2.682 (10) Å.

The two  $\{\text{SCH}_2\text{CH}_2\}_3\text{N}$  ligands show the typical 'trigonal' arrangement seen in most other metal- $(\{\text{SCH}_2\text{CH}_2\}_3\text{N})$  complexes (Davies *et al.*, 2000). There is disorder in one of these ligands, with occupancies of 54 (2) and 46 (2)% for two orientations, rotated by 45 (2)°. This disorder destroys the pseudo-twofold rotation axis through the central tetrahedral Fe atom; in the unsolvated crystal structure, the two  $\text{Fe}(\{\text{SCH}_2\text{CH}_2\}_3\text{N})(\text{CO})$  units are related by a crystallographic

twofold symmetry axis, but the dimensions of the two complex molecules are very similar and the structure of the minor disorder component of (I) is essentially identical to that of the symmetrical structure. There is also disorder in the benzene solvent molecule, fully resolved, with occupancies of 61 (3) and 39 (3)% for two planes, rotated by approximately 30° and tilted with respect to each other by 16.4 (10)°.

Bond distances within each Fe( $\{\text{SCH}_2\text{CH}_2\}_3\text{N}\}\text{(CO)}$ ) unit are comparable to those in many five-coordinate metal- $\{\text{SCH}_2\text{CH}_2\}_3\text{N}\}$  complexes that we have reported (Davies *et al.*, 2000). The average Fe–S bond length is 2.24 (2) Å for the trigonal bipyramidal Fe atoms and 2.2877 (5) Å for the tetrahedral Fe atoms. S–C bond lengths are 1.822 (9) Å,  $M$ –S–C angles are 99.2 (3) and 106.9 (3)° for the trigonal bipyramidal and tetrahedral irons respectively, and  $M$ –N–C angles are 110.5 (2)°.

## Experimental

To a solution of nickel(II) 2,4-pentanedionate (0.49 g, 1.91 mmol) in benzene (50 ml) was added tris(2-mercaptoethyl)amine (0.40 g, 2.06 mmol) under an atmosphere of dinitrogen. After vigorous stirring for 30 min, a brown precipitate was removed by filtration. The filtrate was allowed to stand for 3 d, during which time dark-purple rosettes of previously reported (Davies *et al.*, 1999)  $[\text{Ni}\{\{\text{SCH}_2\text{CH}_2\}_2\text{N}(\text{CH}_2\text{CH}_2\text{SH})\}]_2$  formed. The crystals were removed by filtration; to the filtrate was added iron pentacarbonyl (1.49 g, 7.61 mmol) and the mixture left to stand for a further 3 d. The dark crystalline needles which formed were collected by filtration, washed repeatedly with diethyl ether and dried *in vacuo*. Expected for  $\text{C}_{20}\text{H}_3\text{Fe}_3\text{N}_2\text{O}_2\text{S}_6$ : C 34.8, H 4.4, N 4.1, Fe 24.3%; found: C 34.9, H 4.6, N 3.8, Fe 24.0%.  $\nu(\text{CO})$  1952  $\text{cm}^{-1}$ . Mössbauer (solid, 77 K, ref. iron foil 298 K), two doublets, relative intensity 2:1:  $\delta_1 = 0.20$ ,  $\Delta E_{q1} = 1.15$ ,  $\Gamma_{1/2} = 0.13$   $\text{mm s}^{-1}$ ;  $\delta_2 = 0.59$ ,  $\Delta E_{q2} = 1.98$ ,  $\Gamma_{1/2} = 0.13$   $\text{mms}^{-1}$ .

### Crystal data

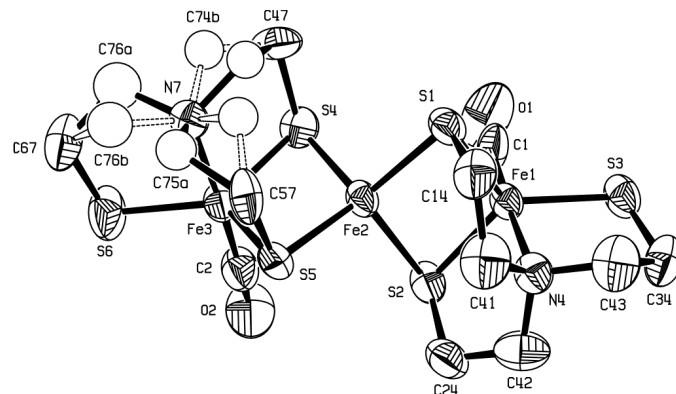
$[\text{Fe}_3(\text{C}_6\text{H}_{12}\text{NS}_3)_2(\text{CO})_2] \cdot \text{C}_6\text{H}_6$	$D_x = 1.655$ $\text{Mg m}^{-3}$
$M_r = 690.37$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 24 reflections
$a = 14.1644$ (12) Å	$\theta = 10$ – $11^\circ$
$b = 11.0663$ (15) Å	$\mu = 2.02$ $\text{mm}^{-1}$
$c = 17.820$ (2) Å	$T = 293$ (2) K
$\beta = 97.226$ (8)°	Rectangular prism, orange–brown
$V = 2771.1$ (6) Å <sup>3</sup>	$0.74 \times 0.13 \times 0.10$ mm
$Z = 4$	

### Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.058$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 24.0^\circ$
Absorption correction: $\psi$ scan (EMPABS; Sheldrick <i>et al.</i> , 1977)	$h = -1 \rightarrow 16$
$T_{\text{min}} = 0.914$ , $T_{\text{max}} = 0.960$	$k = -1 \rightarrow 12$
5226 measured reflections	$l = -20 \rightarrow 20$
4356 independent reflections	3 standard reflections
1873 reflections with $I > 2\sigma(I)$	every 300 reflections
	frequency: 167 min
	intensity decay: none

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.057$	$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$
$wR(F^2) = 0.144$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4356 reflections	$\Delta\rho_{\text{max}} = 0.59$ $\text{e \AA}^{-3}$
291 parameters	$\Delta\rho_{\text{min}} = -0.47$ $\text{e \AA}^{-3}$



**Figure 1**

A view of (I). Displacement ellipsoids are drawn at the 50% probability level. The C atoms in the disordered  $\{\text{SCH}_2\text{CH}_2\}_3\text{N}$  ligand on Fe3, which were refined isotropically, are shown as spheres. The benzene of solvation has been omitted.

**Table 1**

Selected geometric parameters (Å, °).

Fe1–C1	1.708 (13)	Fe2–S5	2.276 (3)
Fe1–N4	2.043 (8)	Fe2–S4	2.298 (3)
Fe1–S3	2.214 (3)	Fe2–Fe3	2.6721 (18)
Fe1–S2	2.243 (3)	Fe3–C2	1.743 (11)
Fe1–S1	2.272 (3)	Fe3–N7	2.054 (7)
Fe1–Fe2	2.6917 (18)	Fe3–S6	2.209 (3)
S1–Fe2	2.281 (3)	Fe3–S5	2.256 (3)
S2–Fe2	2.295 (3)	Fe3–S4	2.260 (3)
C1–O1	1.150 (12)	C2–O2	1.148 (11)
C1–Fe1–N4	174.7 (4)	Fe3–Fe2–Fe1	164.28 (7)
C1–Fe1–S3	87.0 (3)	C2–Fe3–N7	176.5 (4)
N4–Fe1–S3	88.1 (2)	C2–Fe3–S6	88.5 (3)
C1–Fe1–S2	93.6 (4)	N7–Fe3–S6	88.0 (2)
N4–Fe1–S2	87.8 (2)	C2–Fe3–S5	94.5 (4)
S3–Fe1–S2	127.13 (11)	N7–Fe3–S5	87.5 (2)
C1–Fe1–S1	95.7 (4)	S6–Fe3–S5	125.40 (13)
N4–Fe1–S1	88.7 (2)	C2–Fe3–S4	93.8 (4)
S3–Fe1–S1	125.14 (11)	N7–Fe3–S4	88.3 (2)
S2–Fe1–S1	107.43 (10)	S6–Fe3–S4	126.39 (14)
O1–C1–Fe1	176.6 (10)	S5–Fe3–S4	107.83 (11)
S5–Fe2–S1	116.63 (11)	O2–C2–Fe3	177.7 (10)
S5–Fe2–S2	107.48 (10)	Fe1–S1–Fe2	72.48 (8)
S1–Fe2–S2	105.37 (10)	Fe1–S2–Fe2	72.75 (8)
S5–Fe2–S4	105.88 (11)	Fe3–S4–Fe2	71.79 (9)
S1–Fe2–S4	108.38 (11)	Fe3–S5–Fe2	72.26 (9)
S2–Fe2–S4	113.33 (10)		
S1–C14–C41–N4	49.3 (10)	S5–C57–C75A–N7	–48.4 (14)
S2–C24–C42–N4	44.8 (11)	S5–C57–C75B–N7	50.6 (15)
S3–C34–C43–N4	49.8 (11)	S6–C67–C76A–N7	–49.2 (18)
S4–C47–C74A–N7	–47.3 (15)	S6–C67–C76B–N7	45.4 (19)
S4–C47–C74B–N7	41.9 (19)		

Intensity data were collected to  $\theta_{\text{max}}$  of 25°, giving maximum  $hkl$  indices of 16, 13 and 21, and 4865 unique reflections, of which 1899 were observed; those greater than 24° were found to be rather weak and unreliable and were not used in the final refinement. Negative intensities were eliminated using BAYES (French & Wilson, 1978), before structure solution and refinement.

The structure analysis indicated regions of disorder in the solvent benzene molecule and in the N-bonded C atoms of one of the  $\{\text{SCH}_2\text{CH}_2\}_3\text{N}$  ligands in the complex. All atomic sites in the disordered regions of the structure were unambiguously located from electron-density maps and were well resolved. However, the limitations of the data ( $\theta$  maximum of 24°, collection at room temperature, *etc.*) yield less-than-perfect results with a wide range of bond lengths

and angles in the disordered regions. During the refinement process, geometrical restraints were applied to the disordered regions [*viz.* N—C = 1.49 (1) Å and C—C = 1.50 (1) Å in the anion, and C—C = 1.39 (1) Å in the benzene molecule], but the *R* factors were higher, with no significant changes to the rest of the structure. Finally, all atoms were allowed to refine freely in order to give a more reliable indication of the accuracy and quality of the model based on the crystallographic data.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *CAD-4 Processing Program* (Hursthouse, 1976); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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