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1,3-Bis(diphenylphosphino)propane-2κ^2*P*,*P*′-{μ-2-[bis(2-mercaptoethyl)amino]ethanesulfinato(3−)-1κ^4*N*,*S*,*S*′,*S*″:2κ^2*S*,*S*′}chloro-2κ*Cl*-dinitroso-1κ^2*N*-iron(II)nickel(II) acetonitrile hemisolvate

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Key indicators

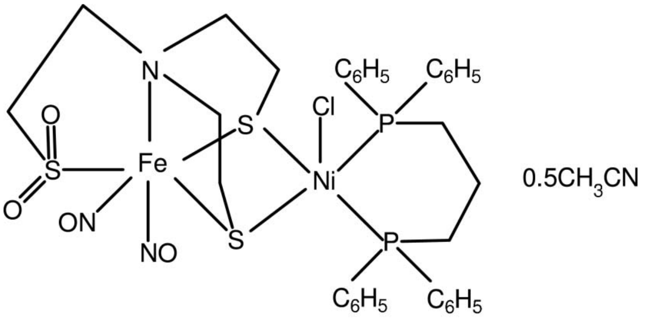
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.019 Å
H-atom completeness 97%
R factor = 0.108
wR factor = 0.256
Data-to-parameter ratio = 30.5

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

The title compound, [{Fe[($SO_2CH_2CH_2$)(SCH_2CH_2)$_2$N]-(NO)$_2$-*S*,*S*′}NiCl{[P(C_6H_5)$_2$]$_2$(CH_2)$_3$}]·0.5CH_3CN or [FeNi($C_6H_{12}NO_2S_3$)Cl($C_{27}H_{26}P_2$)(NO)$_2$]·0.5C_2H_3N, is described. There are two crystallographically distinct dimetallic complex molecules. In each molecule, the Fe atom is octahedrally coordinated, with the three S atoms and an N atom of one of the two NO ligands forming the equatorial plane; the N atoms from the second NO group and the ($SO_2CH_2CH_2$)-(SCH_2CH_2)$_2$N ligand lie in the axial positions. The Ni atom is square pyramidally coordinated by the two bridging S atoms and the two P atoms forming the basal plane, and by the Cl atom lying in the apical position. Slight differences in the bonding modes of the NO ligands are observed for the two distinct molecules.

Comment

As part of our studies on the synthesis of dimetallic complexes with structural properties related to the active site of the enzyme nickel–iron hydrogenase (Evans & Pickett, 2003), we have been exploring the utility of the anion [Fe{(SCH_2CH_2)$_3$N}(NO)]$^-$ as a synthon (Davies *et al.*, 2002; Smith *et al.*, 2002; Smith *et al.*, 2003). The title compound, (I), crystallized as an unexpected minor product after long-term storage of a solution in acetonitrile at 277 K, from the attempted preparation of [{Fe[(SCH_2CH_2)$_3$N](NO)-*S*,*S*′}NiCl-{[P(C_6H_5)$_2$]$_2$(CH_2)$_3$}] following an adaptation of the method established for a related complex (Smith *et al.*, 2002).



(I)

The asymmetric unit of (I) contains two complex molecules, denoted *A* (containing Fe and Ni) and *B* (Fe1*b* and Ni1*b*), and one CH_3CN solvent molecule, the latter showing signs of disorder (Fig. 1).

The structures of *A* and *B* in (I) closely resemble those of the analogous species in [{Fe[(SCH_2CH_2)$_3$N](CO)$_2$-*S*,*S*′}NiCl{[P(C_6H_5)$_2$]$_2$(CH_2)$_3$}], (II) (Duff *et al.*, 2005), with bond dimensions similar in both. In (I), both Fe atoms are

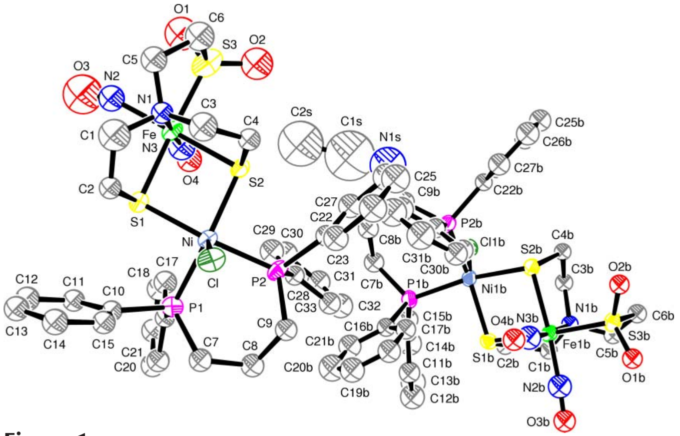


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids (H atoms have been omitted for clarity).

octahedrally coordinated, with the three S atoms and the N atom of one of the NO ligands forming the equatorial plane, while the N atoms from the $(SO_2CH_2CH_2)(SCH_2CH_2)_2N$ and second NO ligand lie in the axial positions. The Fe atoms lie 0.119 (2) and 0.045 (2) Å from the mean equatorial planes in molecules *A* and *B*, respectively, and are displaced towards the axial NO ligands. The Ni atoms are square pyramidally coordinated with an S_2P_2 base plane and the Cl atom lying in the apical position. The Ni atoms lie 0.297 (2) and 0.328 (2) Å from the mean base planes for molecules *A* and *B*, respectively, displaced towards the Cl atoms. The angle between the normals to the mean equatorial and base planes are 167.35 (8) and 159.69 (8)° for *A* and *B*, respectively, with Fe$\cdots$Ni distances of 3.372 (2) and 3.343 (2) Å.

Bond distances about the metal atoms are not unusual (Table 1); within the core of the $(SO_2CH_2CH_2)(SCH_2CH_2)_2N$ ligand and in the $[P(C_6H_5)_2]_2(CH_2)_3$ ligand, dimensions are as found in (II), including the removal of the usual pseudo-threefold rotation about the *M*—N axis of $(SCH_2CH_2)_3N$ and related ligands by the non-bridging SCH_2CH_2 group. Three of the NO ligands are classed as being 'linear' (Table 2), while the equatorial NO in molecule *A* may be described as 'bent'. The configuration is different in (II), where both CO ligands in the two independent molecules are linear, as expected, with *M*—C—O bond angles of 175.3 (5) and 176.9 (5)° in one molecule, and 175.4 (8) and 176.9 (5) Å in the second.

The component molecules in (I) are arranged within the crystal structure with normal van der Waals contacts between the individual components.

Experimental

Under a dinitrogen atmosphere, $(NEt_4)[Fe\{(SCH_2CH_2)_3N\}(NO)]$ (0.12 g, 0.29 mmol) was added to a stirred solution of $[NiCl_2(dppp)]$ (0.16 g, 0.29 mmol) in MeCN (75 ml). The reaction mixture was stirred overnight. Some red–brown precipitate was removed by filtration and the filtrate stored for eight months at 277 K. After this time, a few red crystals of (I) were collected by filtration. ν(NO), KBr: 1704 and 1733 cm^{-1}; Mössbauer (solid, 80 K, relative to iron foil at 298 K) isomer shift 0.26 mm s^{-1}, quadrupole splitting 1.19 mm s^{-1}.

Crystal data

$[FeNi(C_6H_{12}NO_2S_3)Cl(C_{27}H_{26}P_2)(NO)_2]\cdot 0.5C_2H_3N$
$M_r = 869.32$
Monoclinic, $P2_1/n$
$a = 16.5125$ (5) Å
$b = 17.8156$ (6) Å
$c = 25.5801$ (8) Å
$\beta = 99.913$ (2)°
$V = 7412.8$ (4) Å^3
$Z = 8$
$D_x = 1.558$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 52202 reflections
$\theta = 3.4$–26.0°
$\mu = 1.27$ mm^{-1}
$T = 173$ (2) K
Prism, red
0.10 × 0.05 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.864$, $T_{max} = 0.975$
52202 measured reflections
14540 independent reflections
7005 reflections with $I > 2\sigma(I)$
$R_{int} = 0.155$
$\theta_{max} = 26.0°$
$h = -20 \rightarrow 18$
$k = -20 \rightarrow 21$
$l = -31 \rightarrow 31$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.108$
$wR(F^2) = 0.256$
$S = 0.99$
14540 reflections
477 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0679P)^2 + 96.5506P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.63$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Ni—S1	2.248 (3)	Ni1*b*—S1*b*	2.253 (3)
Ni—S2	2.243 (3)	Ni1*b*—S2*b*	2.259 (3)
Ni—P1	2.205 (3)	Ni1*b*—P1*b*	2.193 (3)
Ni—P2	2.201 (3)	Ni1*b*—P2*b*	2.203 (3)
Ni—Cl	2.607 (3)	Ni1*b*—Cl1*b*	2.560 (3)
Fe—N1	2.039 (9)	Fe1*b*—N1*b*	2.052 (9)
Fe—N2	1.991 (12)	Fe1*b*—N2*b*	1.794 (12)
Fe—N3	1.760 (12)	Fe1*b*—N3*b*	1.781 (12)
Fe—S1	2.305 (3)	Fe1*b*—S1*b*	2.290 (3)
Fe—S2	2.284 (3)	Fe1*b*—S2*b*	2.293 (3)
Fe—S3	2.222 (5)	Fe1*b*—S3*b*	2.224 (3)

Table 2
Bond lengths (Å) and angles (°) in idealized NO ligands and in complex (I).

			Molecule *A*		Molecule *B*	
	Bent	Linear	Equatorial	Axial	Equatorial	Axial
M—N—O	149	175	149.1 (14)	175.1 (10)	176.4 (10)	177.3 (10)
M—N	1.992	1.759	1.991 (12)	1.759 (12)	1.779 (12)	1.794 (12)
N—O	1.023	1.177	1.023 (16)	1.177 (12)	1.157 (12)	1.158 (12)

The crystal of (I) was a very weak scatterer, particularly at higher angles. All C, N and O atoms were refined isotropically. H atoms were positioned geometrically (C—H = 0.95–0.99 Å) and refined as riding [$U_{iso}(H) = 1.2U_{eq}(C)$]. The H atoms of the solvent molecule were not located. The highest peak is located 0.96 Å from atom O3.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor 1997)and *SCALEPACK*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular

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graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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