Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

1,3-Bis(diphenylphosphino)propane-2κ^2*P*,*P*′-dicarbonyl-1κ^2*C*-chloro-2κ*Cl*-{μ-2,2′,2″-nitrilotriethanethiolato(3−)-1κ^4*N*,*S*,*S*′,*S*″:2κ^2*S*,*S*′}-iron(II)nickel(II) acetonitrile solvate

S. E. Duff,[a] P. B. Hitchcock,[b] S. C. Davies,[a] J. E. Barclay[a] and D. J. Evans[a]*

[a]Department of Biological Chemistry, John Innes Centre, Norwich Research Park, Colney, Norwich NR4 7UH, England, and [b]Department of Chemistry, University of Sussex, Falmer, Brighton BN1 9QJ, England

Correspondence e-mail: dave.evans@bbsrc.ac.uk

Received 20 May 2005
Accepted 7 June 2005
Online 17 June 2005

The structure of the neutral title complex, [{Fe[(SCH$_2$CH$_2$)$_3$N](CO)$_2$-*S*,*S*′}NiCl{[P(C$_6$H$_5$)$_2$]$_2$(CH$_2$)$_3$}]·CH$_3$CN or [FeNi(C$_6$H$_{12}$NS$_3$)Cl(C$_{27}$H$_{26}$P$_2$)(CO)$_2$]·C$_2$H$_3$N, is described. There are two independent complex molecules and two solvent molecules in the asymmetric unit. The Fe atoms are octahedrally coordinated; the three S atoms and a C atom of one of the two CO ligands form the equatorial plane, with the N atom of the (SCH$_2$CH$_2$)$_3$N ligand and the second carbonyl C atom lying in the axial positions. The Ni atoms are square pyramidally coordinated, with the two bridging S atoms and the P atoms of the 1,3-bis(diphenylphosphino)propane ligand forming the basal plane and the Cl atom lying in the apical position.

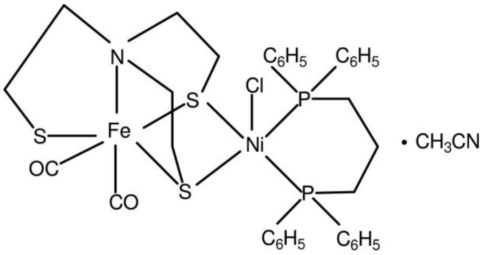
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.009 Å
H-atom completeness 93%
R factor = 0.052
wR factor = 0.107
Data-to-parameter ratio = 11.6

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

Comment

The title compound, (I), was prepared as a further example of a synthetic structural analogue of the dimetallic active site of the enzyme nickel–iron hydrogenase (Evans & Pickett, 2003; Davies *et al.*, 1999; Smith *et al.*, 2002, 2003). Compound (I) is closely related to [{Fe[(SCH$_2$CH$_2$)$_3$N](CO)$_2$-*S*,*S*′}NiCl{[P(C$_6$H$_5$)$_2$]$_2$(CH$_2$)$_2$}], (II) (Davies *et al.*, 1999; Smith *et al.*, 2002), in which the chelating diphosphane is 1,2-bis(diphenylphosphino)ethane (dppe), whereas in (I) it is 1,3-bis(diphenylphosphino)propane (dppp).



(I)

The asymmetric unit consists of two complex molecules and two solvent molecules. The S$_3$C equatorial planes of the octahedrally coordinated Fe atoms are slightly distorted, with deviations from the mean planes lying in the range −0.069 (3) to 0.074 (3) Å in molecule 1 (the negative sign indicates the opposite side of the mean plane) and −0.060 (3) to 0.063 (3) Å in molecule 2. The Fe atoms are displaced from these mean equatorial planes by 0.067 (2) and 0.1400 (12) Å, respectively, towards the axial CO ligand. The S$_2$P$_2$ basal planes of the square pyramidally coordinated Ni atoms are also slightly distorted, with deviations from the mean planes lying in the range −0.054 (3) to 0.053 (3) Å in molecule 1 and −0.035 (3) to 0.035 (3) Å in molecule 2. The Ni atoms are displaced 0.3227 (13) and 0.3175 (14) Å, respectively, from these mean

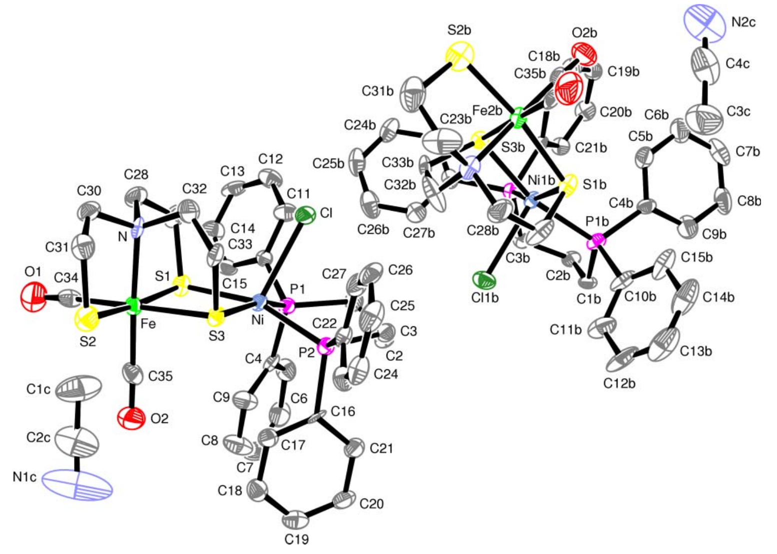
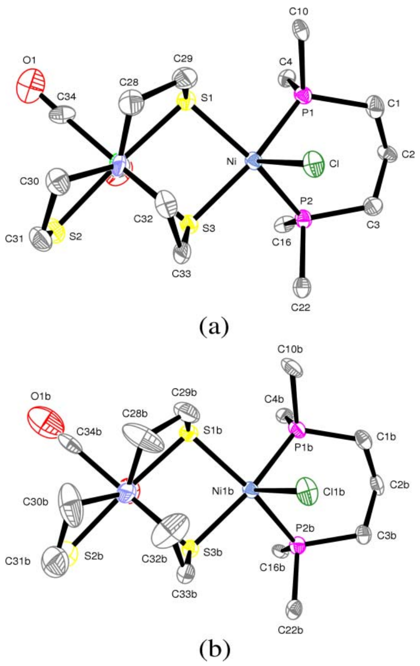


Figure 1
The asymmetric unit of (I), showing displacement ellipsoids at the 50% probability level. H atoms have been omitted.

planes, towards the Cl atoms. The S_3C and S_2P_2 mean planes are not coplanar, with an angle between their normals of 16.31 (6)°; in (II), this angle is 19.38 (7)°.

Bond dimensions about the Fe and Ni atoms are not unusual and are comparable to those in (II) [see Table 1 for dimensions in (I)]. The Fe—C bond to the equatorial CO ligand is slightly longer than those to the axial CO ligand in both molecules of (I) and in complex (II); in the second molecule of (I) it is longer than in the first and in (II) as a result of unresolved disorder in the O atom [Fe—C_{eq} = 1.783 (12) Å and $\text{Fe—C}_{\text{axial}}$ = 1.741 (10) in (II)].



(a)

(b)

Figure 2
View along the N—Fe—C—O axis of (*a*) molecule 1 and (*b*) molecule 2, showing the deviation from the pseudo-threefold rotation of the $(SCH_2CH_2)_3N$ ligand. H atoms have been omitted.

The unusual torsion angles in the $(SCH_2CH_2)_3N$ ligand in (I) are also found in (II); the usual pseudo-threefold rotation about the Fe—N bond is removed by the non-bridging SCH_2CH_2 'arm' in both structures (see Fig. 2). Other bond dimensions in the ligands are as expected.

The molecules are arranged within the crystal structure with the complex molecules forming chains parallel to the crystallographic *a* axis; the solvent molecules occupy the centres of the channels enclosed by four such chains (see Fig. 3).

Experimental

Under an atmosphere of carbon monoxide, a mixture of $[NiCl_2(dppp)]$ (0.21 g, 0.39 mmol) and $(NEt_4)[Fe\{(SCH_2CH_2)_3N\}(CO)]$ (0.16 g, 0.39 mmol) in MeCN (100 ml) was refluxed with stirring for 2.5 h. After cooling overnight, crystals were collected by filtration and dried (0.31 g, 97%). Analysis expected for $C_{37}H_{41}ClFeN_2NiO_2P_2S_3$: C 52.1, H 4.8, N 3.3%; found C 51.7, H 4.9, N 3.2%. ν(CO), KBr: 1944 and 2006 cm^{-1}; Mössbauer (solid, 80 K, relative to iron foil at 298 K) isomer shift 0.07 mm s^{-1}, quadrupole splitting 0.56 mm s^{-1}.

Crystal data

$[FeNi(C_6H_{12}NS_3)Cl(C_{27}H_{26}P_2)(CO)_2]\cdot C_2H_3N$
M_r = 853.85
Orthorhombic, $Pca2_1$
a = 20.6025 (4) Å
b = 12.4769 (2) Å
c = 29.7090 (6) Å
V = 7636.9 (2) $Å^3$
Z = 8

D_x = 1.485 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 24708 reflections
θ = 3.7–23.8°
μ = 1.23 mm^{-1}
T = 173 (2) K
Plate, brown
0.2 × 0.2 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min}$ = 0.823, $T_{\max}$ = 0.979
24708 measured reflections
10246 independent reflections

8837 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
$\theta_{\max}$ = 23.7°
$h = -22 \rightarrow 22$
$k = -14 \rightarrow 13$
$l = -27 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.107$
$S = 1.07$
10246 reflections
884 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2)$
$+ 30.7123P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}
Absolute structure: Flack (1983), 4317 Friedel pairs
Flack parameter: 0.604 (14)

Table 1
Selected geometric parameters (Å, °).

Ni—P1	2.2012 (14)	Ni1*b*—P1*b*	2.2018 (15)
Ni—P2	2.2060 (15)	Ni1*b*—P2*b*	2.2046 (15)
Ni—S3	2.2517 (13)	Ni1*b*—S1*b*	2.2495 (16)
Ni—S1	2.2574 (15)	Ni1*b*—S3*b*	2.2536 (14)
Ni—Cl	2.5787 (14)	Ni1*b*—Cl1*b*	2.5971 (16)
Fe—C35	1.759 (6)	Fe2*b*—C35*b*	1.760 (6)
Fe—C34	1.829 (6)	Fe2*b*—C34*b*	1.912 (7)
Fe—N	2.048 (4)	Fe2*b*—N1*b*	2.065 (5)
Fe—S1	2.2865 (15)	Fe2*b*—S2*b*	2.2839 (19)
Fe—S2	2.2978 (16)	Fe2*b*—S1*b*	2.2909 (16)
Fe—S3	2.3159 (15)	Fe2*b*—S3*b*	2.3029 (15)
O1—C34	1.065 (7)	O1*b*—C34*b*	0.861 (8)
O2—C35	1.151 (7)	O2*b*—C35*b*	1.137 (7)
P1—Ni—P2	92.88 (5)	O2—C35—Fe	176.9 (5)
P1—Ni—S3	165.43 (6)	P1*b*—Ni1*b*—P2*b*	92.84 (6)
P2—Ni—S3	88.90 (5)	P1*b*—Ni1*b*—S1*b*	87.92 (6)
P1—Ni—S1	87.87 (5)	P2*b*—Ni1*b*—S1*b*	161.55 (6)
P2—Ni—S1	160.38 (6)	P1*b*—Ni1*b*—S3*b*	164.85 (6)
S3—Ni—S1	85.67 (5)	P2*b*—Ni1*b*—S3*b*	88.78 (5)
P1—Ni—Cl	88.51 (5)	S1*b*—Ni1*b*—S3*b*	85.85 (5)
P2—Ni—Cl	92.94 (5)	P1*b*—Ni1*b*—Cl1*b*	88.79 (5)
S3—Ni—Cl	105.85 (5)	P2*b*—Ni1*b*—Cl1*b*	92.29 (5)
S1—Ni—Cl	106.68 (5)	S1*b*—Ni1*b*—Cl1*b*	106.16 (6)
C35—Fe—C34	91.6 (2)	S3*b*—Ni1*b*—Cl1*b*	106.21 (5)
C35—Fe—N	175.2 (2)	C35*b*—Fe2*b*—C34*b*	90.1 (3)
C34—Fe—N	92.5 (2)	C35*b*—Fe2*b*—N1*b*	177.9 (2)
C35—Fe—S1	95.72 (19)	C34*b*—Fe2*b*—N1*b*	91.8 (2)
C34—Fe—S1	96.10 (18)	C35*b*—Fe2*b*—S2*b*	94.41 (19)
N—Fe—S1	86.26 (12)	C34*b*—Fe2*b*—S2*b*	87.86 (18)
C35—Fe—S2	90.91 (19)	N1*b*—Fe2*b*—S2*b*	86.57 (13)
C34—Fe—S2	87.63 (18)	C35*b*—Fe2*b*—S1*b*	92.44 (18)
N—Fe—S2	86.83 (12)	C34*b*—Fe2*b*—S1*b*	95.97 (18)
S1—Fe—S2	172.29 (7)	N1*b*—Fe2*b*—S1*b*	86.47 (13)
C35—Fe—S3	88.34 (18)	S2*b*—Fe2*b*—S1*b*	172.15 (7)
C34—Fe—S3	179.60 (19)	C35*b*—Fe2*b*—S3*b*	90.78 (19)
N—Fe—S3	87.58 (12)	C34*b*—Fe2*b*—S3*b*	179.1 (2)
S1—Fe—S3	83.53 (5)	N1*b*—Fe2*b*—S3*b*	87.29 (13)
S2—Fe—S3	92.76 (6)	S2*b*—Fe2*b*—S3*b*	92.30 (6)
Ni—S1—Fe	95.51 (6)	S1*b*—Fe2*b*—S3*b*	83.76 (5)
O1—C34—Fe	175.3 (5)	Ni1*B*—S1*B*—Fe2*B*	95.18 (6)
Fe—S1—C29—C28	−9.4 (6)	C29*b*—C28*b*—N1*b*—Fe2*b*	−43.0 (10)
S1—C29—C28—N	38.6 (8)	Fe2*b*—S2*b*—C31*b*—C30*b*	25.8 (8)
C29—C28—N—Fe	−51.9 (7)	S2*b*—C31*b*—C30*b*—N1*b*	−54.9 (10)
Fe—S2—C31—C30	23.7 (6)	C31*b*—C30*b*—N1*b*—Fe2*b*	58.7 (9)
S2—C31—C30—N	−51.7 (8)	Fe2*b*—S3*b*—C33*b*—C32*b*	−35.8 (7)
C31—C30—N—Fe	55.3 (7)	S3*b*—C33*b*—C32*b*—N1*b*	42.1 (10)
Fe—S3—C33—C32	−38.3 (6)	C33*b*—C32*b*—N1*b*—Fe2*b*	−24.5 (10)
S3—C33—C32—N	45.8 (8)	P1—C1—C2—C3	−68.5 (8)
C33—C32—N—Fe	−27.3 (8)	C1—C2—C3—P2	69.7 (8)
Fe2*b*—S1*b*—C29*b*—C28*b*	−3.0 (8)	P1*b*—C1*b*—C2*b*—C3*b*	−69.3 (8)
S1*b*—C29*b*—C28*b*—N1*b*	29.6 (12)	C1*b*—C2*b*—C3*b*—P2*b*	67.1 (8)

H atoms were not located for the CH_3CN solvent molecules. The value of the Flack (1983) parameter indicates an inversion twin. All other H atoms were positioned geometrically (C—H = 0.95–0.99 Å) and refined as riding [$U_{iso}(H) = 1.2U_{eq}(C)$].

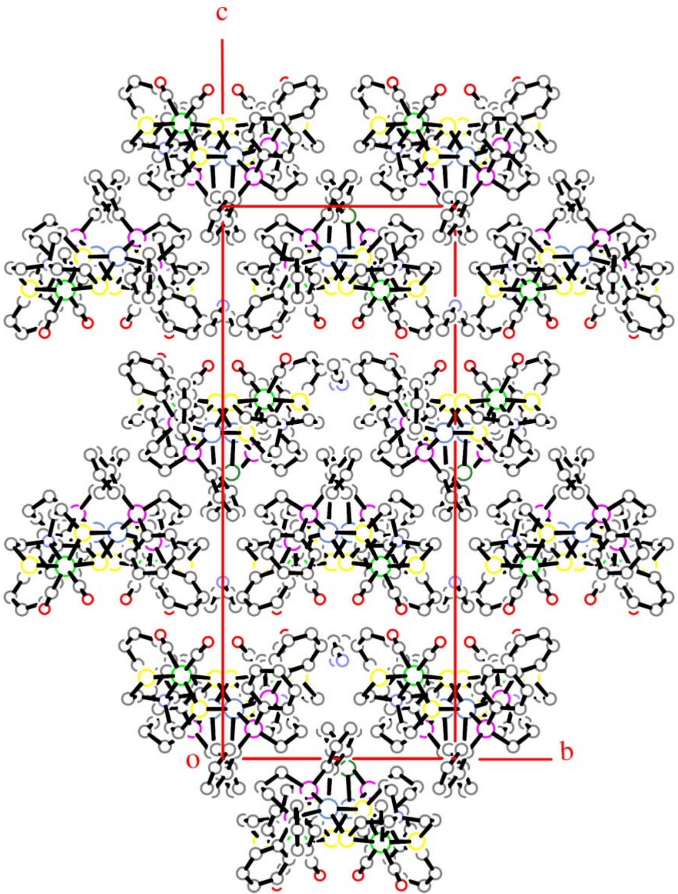


Figure 3
The packing, viewed along the crystallographic *a* axis. Atoms are represented by arbitrary spheres. H atoms have been omitted.

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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors thank the Biotechnology and Biological Sciences Research Council and the John Innes Foundation (SED) for financial support.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Davies, S. C., Evans, D. J., Hughes, D. L., Longhurst, S. & Sanders, J. R. (1999). *Chem. Commun.* pp. 1935–1936.
Evans, D. J. & Pickett, C. J. (2003). *Chem. Soc. Rev.* **32**, 268–275.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Smith, M. C., Barclay, J. E., Cramer, S. P., Davies, S. C., Gu, W.-W., Hughes, D. L., Longhurst, S. & Evans, D. J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2641–2647.

Smith, M. C., Barclay, J. E., Davies, S. C., Hughes, D. L. & Evans, D. J. (2003). *Dalton Trans.* pp. 4147–4151.