[1,2-Bis(diphenylphosphino)ethane-*P*,*P'*]-(4-morpholinecarbodithioato-*S*,*S'*)nickel(II) Perchlorate Dichloromethane Solvate

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Abstract

The crystal structure determination of the title compound, [Ni(C₅H₈NOS₂)(C₂₆H₂₄P₂)]ClO₄.CH₂Cl₂, indicates that the morpholine ring adopts two orientations related by a rotation of 180°. The perchlorate group is highly disordered and forms close contacts with both the morpholino ligand and the dichloromethane solvent molecule. However, there are no short contacts between the dichloromethane solvent and the complex molecule.

Comment

Extensive studies have been carried out on the crystal structures and magnetic properties of 4-morpholinecarbodithioato–metal complexes at room and low temperatures, and with different solvent molecules in the crystal lattice. It has been observed that the morpholine group can be disordered when dichloromethane or benzene are present as solvent molecules; this disorder has been attributed to the ease of loss of the solvent from the crystal lattice. In such cases, short contacts have been observed between the solvent molecule and the disordered morpholino ligand. In some cases, there is also disorder in the solvent molecule itself (Esperas & Husebye, 1975; Healy & Sinn, 1974; Butcher & Sinn, 1975, 1976; Stahl, 1983a,b). In the title compound, (I), disorder is observed in the perchlorate ion, which forms close contacts with the morpholino ligand. The dichloromethane molecule itself does not make any close contacts with the complex molecule but does form close contacts with the perchlorate group. This suggests

that the disorder in the morpholine ring can be induced when either solvent or anionic molecules are in its vicinity. The disorder can be resolved in terms of two separate chair conformations related by a rotation of 180° as shown in Fig. 2.

(I)
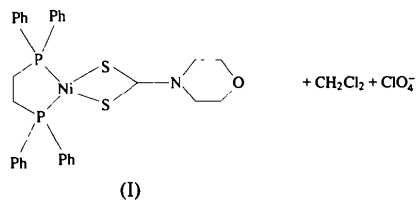
The Ni—P distances [Ni—P1 2.168 (1) and Ni—P2 2.160 (1) Å] are in the same range [2.165 (1)–2.188 (1) Å] as those found in the structure of the [1,2-bis(diisopropylphosphino)ethane]carbenenickel(0) complex (Gabor, Krüger, Marczinke, Mynott & Wilke, 1991). The present P—Ni—P angle [86.81 (4)°], however, is less than that observed in this nickel(0) complex [91.0 (1)°]. Generally, the P—Ni—P angle is greater than 93° for structures incorporating unbridged di- or triphenylphosphine ligands due to steric effects (Ramalingam, Aravamudan & Seshasayee, 1987) and therefore the ethane group may be the cause of the shortening of
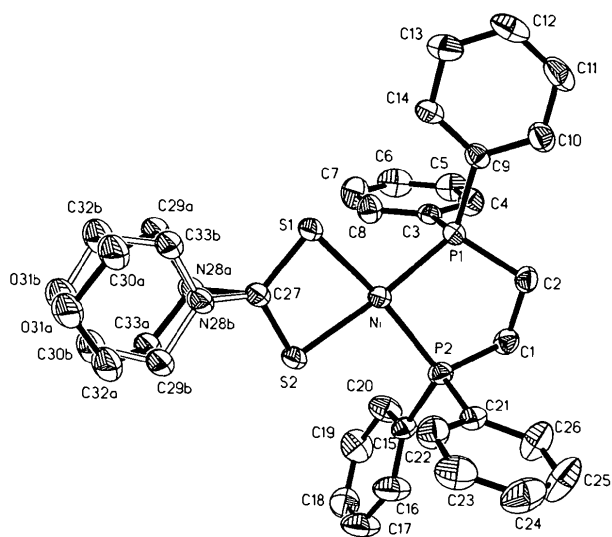

Fig. 1. Structure of the title compound with 30% probability displacement ellipsoids. The disordered perchlorate group, the dichloromethane solvent molecule and the H atoms are omitted for clarity.
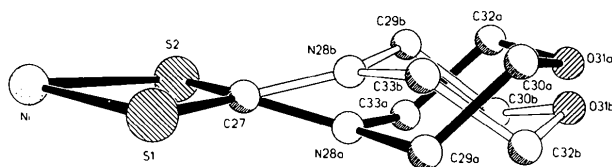

Fig. 2. The 4-morpholinecarbodithioato ligand showing two different orientations of the morpholine ring corresponding to a rotation of 180°.

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the Ni—P bond lengths and the reduction in the P— Ni—P angle. The P—C distances are normal but one of the valence angles around P1 [Ni—P1—C9 125.4 (1)°] deviates from normal values. The bond lengths and angles in the phenyl rings show normal values. The two phenyl groups in each of the diphenylphosphine moieties make dihedral angles of 85.2 (2) and 78.9 (2)° with respect to one another. The Ni atom has distorted square-planar coordination, the maximum deviation from the mean plane being 0.331 (1) Å for atom S2. The Ni—S and S—C bond lengths are normal and do not show any appreciable asymmetic variations.

Experimental

The preparation of the title compound was accomplished by established procedures (Ramalingam, Aravamudan, Seshasayee & Subramanyam, 1984; Ramalingam, Aravamudan & Seshasayee, 1987). The parent dithiocarbamato complex was prepared from morpholinium morpholine-4-carbodithioate and nickel chloride (Aravamudan, Brown & Venkappayya, 1971). Single crystals were obtained from dichloromethane solution by slow evaporation at room temperature.

Crystal data

[Ni(C$_5$H$_8$NOS$_2$)(C$_{26}$H$_{24}$P$_2$)]- ClO$_4$.CH$_2$Cl$_2$
M_r = 803.72
Monoclinic
$P2_1/c$
a = 9.456 (2) Å
b = 22.745 (4) Å
c = 16.707 (3) Å
β = 93.16 (2)°
V = 3587.8 (12) Å^3
Z = 4
D_x = 1.488 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8–15°
μ = 1.010 mm^{-1}
T = 293 (2) K
Needle
0.4 × 0.3 × 0.3 mm
Orange

Data collection

Siemens *P*4 four-circle diffractometer
θ–2θ scans
Absorption correction: none
8522 measured reflections
8245 independent reflections
3962 observed reflections
[I > $2\sigma(I)$]

R_{int} = 0.0358
θ_{max} = 27.57°
h = −12 → 12
k = 0 → 29
l = 0 → 21
3 standard reflections monitored every 100 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R(F)$ = 0.0510
$wR(F^2)$ = 0.1306
S = 0.869
8245 reflections
457 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.002
$\Delta\rho_{max}$ = 0.447 e Å^{-3}
$\Delta\rho_{min}$ = −0.431 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	0.34673 (5)	0.52070 (2)	0.69655 (3)	0.04178 (15)
S1	0.41710 (12)	0.44922 (5)	0.61808 (6)	0.0523 (3)
S2	0.49575 (13)	0.47404 (5)	0.77950 (6)	0.0604 (3)
P1	0.24779 (10)	0.58224 (5)	0.61166 (6)	0.0425 (3)
P2	0.26153 (11)	0.57390 (5)	0.78957 (6)	0.0444 (3)
C1	0.1856 (4)	0.6411 (2)	0.7465 (2)	0.0534 (11)
C2	0.1190 (4)	0.6262 (2)	0.6635 (2)	0.0511 (10)
C3	0.3888 (4)	0.6332 (2)	0.5889 (2)	0.0451 (9)
C4	0.3598 (5)	0.6914 (2)	0.5684 (3)	0.0602 (12)
C5	0.4669 (6)	0.7283 (2)	0.5492 (3)	0.0729 (14)
C6	0.6041 (6)	0.7083 (3)	0.5480 (3)	0.082 (2)
C7	0.6323 (5)	0.6518 (3)	0.5670 (3)	0.081 (2)
C8	0.5265 (4)	0.6133 (2)	0.5876 (3)	0.0625 (12)
C9	0.1658 (4)	0.5631 (2)	0.5137 (2)	0.0446 (9)
C10	0.0389 (4)	0.5863 (2)	0.4862 (3)	0.0631 (12)
C11	−0.0162 (5)	0.5737 (3)	0.4100 (3)	0.081 (2)
C12	0.0576 (6)	0.5377 (3)	0.3611 (3)	0.077 (2)
C13	0.1828 (6)	0.5141 (2)	0.3882 (3)	0.0740 (14)
C14	0.2376 (5)	0.5265 (2)	0.4646 (2)	0.0594 (11)
C15	0.3866 (4)	0.5944 (2)	0.8703 (2)	0.0480 (10)
C16	0.3808 (5)	0.5719 (3)	0.9458 (3)	0.083 (2)
C17	0.4851 (7)	0.5853 (3)	1.0036 (3)	0.098 (2)
C18	0.5920 (6)	0.6221 (3)	0.9887 (3)	0.079 (2)
C19	0.5973 (5)	0.6450 (2)	0.9145 (4)	0.085 (2)
C20	0.4969 (5)	0.6318 (2)	0.8553 (3)	0.0735 (14)
C21	0.1191 (4)	0.5341 (2)	0.8334 (2)	0.0494 (10)
C22	0.1336 (5)	0.4752 (2)	0.8470 (3)	0.0704 (13)
C23	0.0302 (7)	0.4435 (3)	0.8822 (3)	0.085 (2)
C24	−0.0909 (7)	0.4700 (3)	0.9015 (3)	0.098 (2)
C25	−0.1072 (6)	0.5280 (3)	0.8886 (4)	0.114 (2)
C26	−0.0029 (6)	0.5606 (2)	0.8549 (3)	0.089 (2)
C27	0.5140 (5)	0.4263 (2)	0.7019 (2)	0.0583 (12)
N28A	0.6226 (11)	0.3877 (5)	0.7003 (7)	0.053 (2)
C29A	0.6445 (13)	0.3467 (5)	0.6322 (6)	0.067 (2)
C30A	0.6248 (15)	0.2839 (5)	0.6588 (7)	0.086 (2)
O31A	0.720 (5)	0.2714 (19)	0.7301 (26)	0.102 (7)
C32A	0.6869 (15)	0.3075 (5)	0.7916 (8)	0.086 (2)
C33A	0.7088 (12)	0.3713 (5)	0.7738 (6)	0.067 (2)
N28B	0.5647 (11)	0.3712 (5)	0.7115 (7)	0.053 (2)
C29B	0.6286 (11)	0.3497 (5)	0.7882 (6)	0.067 (2)
C30B	0.7746 (14)	0.3265 (6)	0.7765 (8)	0.086 (2)
O31B	0.763 (5)	0.2820 (19)	0.7149 (26)	0.102 (7)
C32B	0.7127 (13)	0.3038 (6)	0.6428 (7)	0.086 (2)
C33B	0.5674 (11)	0.3282 (5)	0.6467 (6)	0.067 (2)
C34	0.1172 (7)	0.2297 (3)	0.2470 (5)	0.141 (3)
Cl1	0.2030 (2)	0.29506 (10)	0.25327 (13)	0.1487 (8)
Cl2	0.2250 (3)	0.16953 (11)	0.2546 (2)	0.1905 (11)
Cl3	−0.0170 (2)	0.21692 (7)	0.50429 (9)	0.0788 (4)
O1	0.1075 (17)	0.1835 (8)	0.4945 (13)	0.164 (9)
O2	−0.0226 (27)	0.2331 (12)	0.4295 (9)	0.197 (11)
O3	0.000 (4)	0.2669 (9)	0.5460 (19)	0.293 (16)
O4	−0.1436 (24)	0.1941 (11)	0.5209 (24)	0.210 (14)
O1A	0.0798 (18)	0.1860 (9)	0.5367 (13)	0.190 (10)
O2A	−0.0090 (22)	0.2697 (9)	0.4744 (23)	0.226 (15)
O3A	−0.0599 (28)	0.2225 (16)	0.5786 (9)	0.242 (13)
O4A	−0.1295 (19)	0.1839 (11)	0.4680 (13)	0.153 (10)

Table 2. *Selected geometric parameters* (Å, °)

Ni—P2	2.1601 (12)	O31A—C32A	1.36 (5)
Ni—P1	2.1679 (11)	C32A—C33A	1.50 (2)
Ni—S2	2.1948 (12)	N28B—C29B	1.47 (2)
Ni—S1	2.2139 (12)	N28B—C33B	1.46 (2)
S1—C27	1.712 (4)	C29B—C30B	1.50 (2)
S2—C27	1.708 (4)	C30B—O31B	1.44 (5)
P1—C3	1.823 (4)	O31B—C32B	1.36 (5)
P1—C9	1.824 (4)	C32B—C33B	1.49 (2)
P1—C2	1.830 (4)	C34—Cl1	1.695 (7)
P2—C15	1.805 (4)	C34—Cl2	1.707 (7)
P2—C21	1.811 (4)	Cl3—O1	1.418 (13)
P2—C1	1.820 (4)	Cl3—O2	1.301 (14)
C1—C2	1.529 (5)	Cl3—O3	1.34 (2)

C27—N28A	1.351 (13)	Cl3—O4	1.35 (2)
C27—N28B	1.347 (13)	Cl3—O1A	1.253 (10)
N28A—C29A	1.49 (2)	Cl3—O2A	1.304 (13)
N28A—C33A	1.48 (2)	Cl3—O3A	1.333 (14)
C29A—C30A	1.51 (2)	Cl3—O4A	1.41 (2)
C30A—O31A	1.48 (5)		
P1—Ni—P2	86.81 (4)	N28A—C29A—C30A	110.0 (9)
P1—Ni—S1	102.69 (4)	O31A—C30A—C29A	109.8 (18)
P2—Ni—S2	93.93 (4)	C32A—O31A—C30A	110 (3)
S1—Ni—S2	79.36 (4)	O31A—C32A—C33A	113.2 (15)
C27—S1—Ni	84.51 (14)	N28A—C33A—C32A	109.4 (10)
C27—S2—Ni	85.21 (14)	C27—N28B—C29B	122.7 (11)
C3—P1—C9	104.1 (2)	C27—N28B—C33B	123.7 (10)
C3—P1—C2	105.3 (2)	C33B—N28B—C29B	113.5 (10)
C9—P1—C2	107.1 (2)	N28B—C29B—C30B	109.9 (9)
C3—P1—Ni	104.67 (13)	O31B—C30B—C29B	107.7 (22)
C9—P1—Ni	125.41 (14)	C32B—O31B—C30B	113 (3)
C2—P1—Ni	108.54 (13)	O31B—C32B—C33B	112.0 (20)
C15—P2—C21	107.4 (2)	N28B—C33B—C32B	109.7 (10)
C15—P2—Cl	107.8 (2)	C11—C34—Cl2	114.6 (4)
C21—P2—Cl	107.1 (2)	O1—Cl3—O2	91.8 (13)
C15—P2—Ni	115.30 (13)	O1—Cl3—O3	115.9 (18)
C21—P2—Ni	109.00 (14)	O1—Cl3—O4	124.8 (14)
Cl—P2—Ni	109.92 (13)	O2—Cl3—O3	104.9 (14)
N28B—C27—S2	123.4 (6)	O2—Cl3—O4	108.5 (17)
N28A—C27—S2	122.4 (6)	O3—Cl3—O4	107.8 (19)
N28B—C27—S1	123.5 (6)	O1A—Cl3—O2A	128.8 (14)
N28A—C27—S1	123.7 (6)	O1A—Cl3—O3A	84.5 (15)
S2—C27—S1	110.8 (2)	O1A—Cl3—O4A	113.6 (14)
C27—N28A—C29A	123.8 (10)	O2A—Cl3—O3A	107.2 (17)
C27—N28A—C33A	122.1 (10)	O2A—Cl3—O4A	112.5 (16)
C33A—N28A—C29A	112.4 (10)	O3A—Cl3—O4A	101.0 (11)

Data collection, cell refinement and data reduction were performed using *XSCANS* (Siemens, 1991). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990*a*) and refined using *SHELXL93* (Sheldrick, 1993). Atoms in the morpholine ring showed very high disorder with unreliable C—C bond lengths (1.12 Å). Moreover, the displacement ellipsoids for all the atoms in the ring were oriented in the same direction, *i.e.* perpendicular to the mean plane of the ring. Hence, it was decided to consider the morpholine ring as two entities with opposite orientations (*A* and *B*) and the occupancies of *A* and *B* were initially refined and then fixed at 0.5. The atoms in *A* and *B* were refined anisotropically with the same U_{ij} values being assigned to the same atom species (N28*A* ≡ N28*B*, O31*A* ≡ O31*B*, C*n*A ≡ C*n*B). The O atoms of the disordered perchlorate group were divided into two sets, each having 0.5 occupancy, and refined anisotropically. The H atoms were fixed geometrically and not refined, but were allowed to ride on those atoms to which they are attached. *SHELXTL/PC* (Sheldrick, 1990*b*) software was used for the molecular graphics and *PARST* (Nardelli, 1983) was used for all other geometrical calculations.

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fac-[Co(C$_5$H$_4$NOS)$_3$].H$_2$O.$\frac{1}{2}$CH$_3$OH and *fac*-[Co(C$_5$H$_4$NOS)$_3$].$\frac{1}{3}$CH$_3$OH

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Abstract

Crystals of tris(2-mercaptopyridine *N*-oxido)cobalt-(III) monohydrate hemimethanol solvate, *fac*-[Co(C$_5$H$_4$NOS)$_3$].H$_2$O.$\frac{1}{2}$CH$_3$OH (1), contain *fac*-[Co(III)(mpo)$_3$] (Hmpo = 2-mercaptopyridine *N*-oxide), H$_2$O and MeOH molecules linked by hydrogen bonds. The asymmetric unit consists of two molecules of the cobalt complex, two water and one methanol molecule. The asymmetric unit of the closely related complex tris(2-mercaptopyridine *N*-oxido)cobalt(III) $\frac{1}{3}$-methanol solvate, *fac*-[Co(C$_5$H$_4$NOS)$_3$].$\frac{1}{3}$CH$_3$OH (2), contains three discrete Co(mpo)$_3$ molecules and one MeOH molecule which is linked to one of the Co(mpo)$_3$ units *via* a hydrogen bond. The Co^{III} complex molecules in (1) and (2) do not differ significantly. Each Co atom is coordinated by an O$_3$S$_3$ donor set which defines a distorted *facial* octahedron. Three mpo ligands are chelated to each Co atom, the average O—Co—S