near vicinity of the Hg atoms; these were attributed to series termination errors arising from incomplete data sets in respect of high-angle scattering by mercury or deficiencies in the calculated absorption factors.

For all compounds, data reduction: *DATR* (Small, 1977); program(s) used to solve structures: *SHELX76* (Patterson) (Sheldrick, 1976); program(s) used to refine structures: *SHELX76*; molecular graphics: *SNOOPI* (Davies, 1983)

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: LI1151). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structural Investigation of Ni^{II} Complexes. XI. Dichlorobis(4-methylpiperidine-*N*)(4-methylpyridine-*N*)nickel(II)

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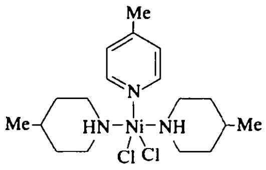
Abstract

Molecules of the title compound, $[NiCl_2(C_6H_7N)(C_6H_{13}N)_2]$, lie on crystallographic twofold axes which pass through each Ni atom and 4-methylpyridine ligand. The coordination polyhedron around the Ni^{II} centre is distorted trigonal bipyramidal with an N_3Cl_2 coordination sphere; the equatorial plane is formed by two chloride ions and the N atom of the 4-methylpyridine ligand, while the axial positions are occupied by the N atoms of the 4-methylpiperidine groups.

Comment

The stoichiometry and stereochemistry of Ni^{II} complexes with various piperidine ligands have been studied. The title compound, $[NiCl_2(4\text{-Mepip})_2(4\text{-Mepy})]$, (I), where 4-Mepip is 4-methylpiperidine and 4-Mepy is 4-methylpyridine, was prepared from the $NiCl_2$/4-Mepip system. The 4-Mepy moiety was formed in the reaction mixture by dehydrogenation (Koman, Ďurčanská, Jóna & Ondrejovič, 1991).



(I)

Spectroscopic and magnetic measurements were consistent with the presence of pentacoordination about the Ni^{II} atom, but could not distinguish between square-pyramidal and trigonal-bipyramidal coordination (Koman, Jóna & Ďurčanská, 1986). Our results show that the coordination polyhedron around the Ni^{II} atom is intermediate between trigonal bipyramidal and square pyramidal (Addison, Rao, Reedijk, Rijn & Verschoor, 1984). Molecules of (I) lie on crystallographic twofold axes (Fig. 1). In the trigonal-bipyramidal complex, the equatorial plane is formed by the N2, Cl and Cl^i atoms [symmetry code: (i) $-x, y, \frac{1}{2} - z$] and the axial ligands are 4-Mepip. In the square-pyramidal complex, two 4-Mepip ligands and two chloride ions define the basal plane, with the apical site occupied by an 4-Mepy ligand. The Ni^{II} ion lies 0.578 (1) Å from this mean basal plane defined by the Cl, Cl^i, N1 and $N1^i$ atoms, in the direction of the N2 atom.

The interatomic distances in the coordination polyhedron of the title complex are in agreement with average interatomic distances in pentacoordinate complexes of nickel(II) with neutral N-donor and chloride ligands (Melník, Šramko, Dunaj-Jurčo, Sirota & Holloway, 1994). Comparison of the Ni—N interatomic distances with those in the complexes $[Ni(NCS)_2(3,5\text{-diMepip})_3]$ (Koman, Jóna & Ďurčanská, 1992), $[Ni(NCS)_2(py)_4]$ (Valach, Sivý & Koreň, 1984), $[Ni(NCS)_2(pip)_4]$ (Koman, Handlovič, Ďurčanská & Gažo, 1983) and $[Ni(NCS)_2(pip)_2(py)(H_2O)].2pip$ (Koman, Ďurčanská, Handlovič & Gažo, 1983) shows that those involving non-aromatic heterocyclic ligands are somewhat longer than those to aromatic ligands.

The $[NiCl_2(4\text{-Mepip})_2(4\text{-Mepy})]$ molecules form layers by means of hydrogen bonding; $N1\cdots Cl^{ii}$ 3.436 (7) Å and $N1—H1\cdots Cl^{ii}$ 168° [symmetry code: (ii) $-x, 1-y, -z$].

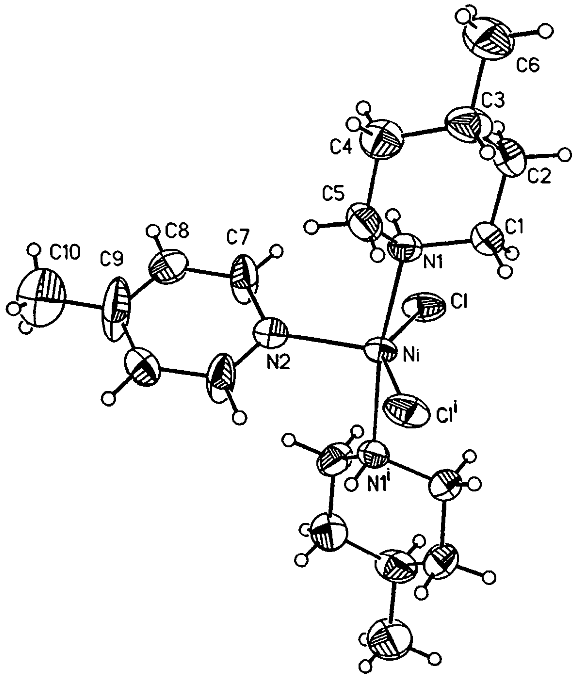


Fig. 1. The molecular structure of $[NiCl_2(4\text{-Mepip})_2(4\text{-Mepy})]$. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as spheres of arbitrary radii.

Experimental

$[NiCl_2(4\text{-Mepip})_2(4\text{-Mepy})]$, (I), was prepared from $NiCl_2$ and 4-Mepip (ratio 1:6) in *o*-xylene. The reaction mixture was stirred under reflux at 417 K for 120 min. The crystals which separated were not very stable at room temperature.

Crystal data

$[NiCl_2(C_6H_7N)(C_6H_{13}N)_2]$
$M_r = 421.08$
Monoclinic
$C2/c$
$a = 20.520\ (4)$ Å
$b = 10.835\ (2)$ Å
$c = 12.333\ (2)$ Å
$\beta = 123.73\ (3)°$
$V = 2280.5\ (7)$ Å^3
$Z = 4$
$D_x = 1.226$ Mg m^{-3}
$D_m = 1.26$ Mg m^{-3}
D_m measured by flotation in C_6H_6/CH_2Cl_2 solution

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4.7–11.9°$
$\mu = 1.090$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.45 × 0.35 × 0.29 mm
Green

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
710 measured reflections
679 independent reflections
672 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0245$

$\theta_{max} = 24.57°$
$h = -16 \rightarrow 22$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 0$
2 standard reflections every 100 reflections intensity decay: 15%

Refinement

Refinement on F^2
$R(F) = 0.0373$
$wR(F^2) = 0.1022$
$S = 1.106$
672 reflections
111 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 5.17P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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	0.52866 (13)	0.25	0.0407 (6)
Cl	0.07326 (11)	0.5883 (2)	0.1685 (2)	0.0607 (7)
N1	−0.1015 (3)	0.5425 (5)	0.0562 (4)	0.0432 (14)
C1	−0.1232 (4)	0.6724 (7)	0.0191 (6)	0.054 (2)
C2	−0.1872 (5)	0.6857 (7)	−0.1251 (7)	0.067 (2)
C3	−0.2595 (5)	0.6120 (8)	−0.1667 (7)	0.069 (3)
C4	−0.2364 (4)	0.4819 (8)	−0.1216 (7)	0.065 (2)
C5	−0.1717 (4)	0.4736 (8)	0.0213 (7)	0.063 (2)
C6	−0.3182 (6)	0.6208 (9)	−0.3116 (9)	0.098 (3)
N2	0	0.3396 (8)	0.25	0.053 (2)
C7	0.0089 (7)	0.2753 (8)	0.1619 (9)	0.100 (4)
C8	0.0091 (6)	0.1445 (9)	0.1599 (8)	0.081 (3)
C9	0	0.0740 (12)	0.25	0.123 (7)
C10	0	−0.0611 (11)	0.25	0.144 (8)

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

Ni—N1	2.132 (5)	Ni—Cl	2.317 (2)
Ni—N2	2.048 (9)		
N1—Ni—N2	94.0 (2)	N2—Ni—Cl	106.20 (6)
N1—Ni—N1^i	171.9 (3)	N1^i—Ni—Cl	90.07 (15)
N1—Ni—Cl	87.67 (15)	Cl—Ni—Cl^i	147.59 (12)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The title structure was solved by Patterson methods. The methyl group centred on C10 was disordered and its H atoms were included as two alternative groupings.

Data collection: *Syntex P*2$_1$ *Software* (Syntex, 1973). Cell refinement: *Syntex P*2$_1$ *Software*. Data reduction: *XP*2$_1$ (Pavelčík, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*SR*,1*R*,2*S*)-1-(*tert*-Butylsulfinyl)-2-(hydroxymethyl)ferrocene

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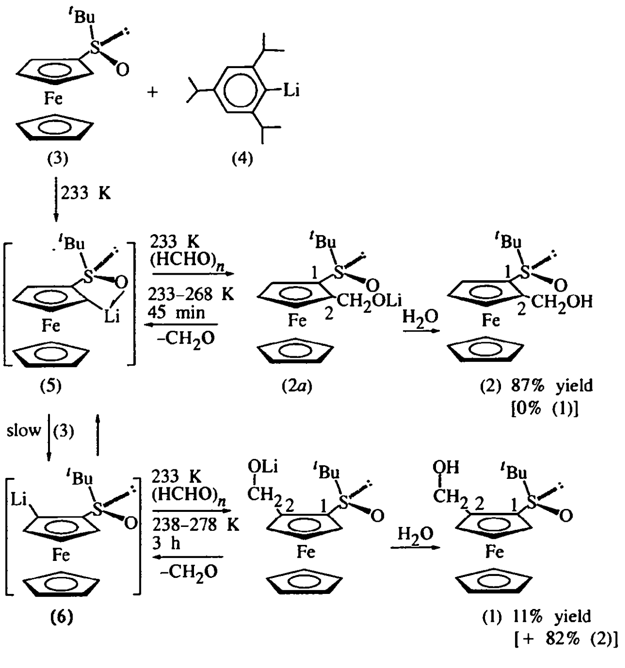
Abstract

From the reaction of (*SR*)-(–)-*tert*-butylsulfinylferrocene with (2,4,6-triisopropylphenyl)lithium followed by paraformaldehyde, the title compound, [Fe(C_5H_5)($C_{10}H_{15}$-O_2S)], was obtained as an unexpected by-product along with the major product, (*SR*,1*S*,2*R*)-2-(*tert*-butylsulfinyl)ferrocenylmethanol. The absolute structure of this by-product could not be ascertained *via* NMR, but it was characterized by X-ray diffraction as (*SR*,1*R*,2*S*)-2-(*tert*-butylsulfinyl)ferrocenylmethanol, a diastereoisomer of the major product. The two cyclopentadienyl rings are rotated away from one another by 25.5 (5)° (from an eclipsed form towards a *gauche* form), in contrast to the mutually eclipsed rings generally found in monosubstituted ferrocenes. Hydrogen bonding between sulfoxide O atoms and hydroxyl H atoms produces infinite one-dimensional chains.

Comment

The regioselective deprotonation of (*SR*)-(–)-*tert*-butylsulfinylferrocene, (3), with (2,4,6-triisopropylphenyl)lithium, (4), provides (*SR*,1*R*,2*S*)-1-(*tert*-butylsulfinyl)-2-lithioferrocene, (5), which reacts with electrophiles to provide a facile and convenient method for the enantioselective synthesis of bidentate ferrocenes with a sulfur-containing substituent (Hua *et al.*, 1996). When the electrophile was paraformaldehyde in this process, (*SR*,1*R*,2*S*)-1-(*tert*-butylsulfinyl)-2-(hydroxymethyl)ferrocene, (2), was isolated in 87% yield [based on reacted (3)] in 45 min. The same reaction with paraformaldehyde carried out at a slightly higher temperature over a 3 h period provided (2) [82% yield based on reacted (3)], along with one of its diastereomers, (1) [11% yield based on reacted (3)]. While the complete structure of (2) was previously determined (Hua *et al.*, 1996), that of (1) remained to be solved. Since this could not be ascertained from ^1H and ^{13}C NMR spectroscopy, an X-ray diffraction study was undertaken.



The X-ray structure of (1) with the atom numbering is shown in Fig. 1. Since the configuration at the S atom would be the same as that of substrate (3), *i.e.* *SR*, the absolute structure of (1) was assigned (*SR*,1*R*,2*S*)-1-(*tert*-butylsulfinyl)-2-(hydroxymethyl)ferrocene and was established by this analysis.